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Optimizing Coagulation-Adsorption for
Haloform and TOC (Total Organic
Carbon) Reduction

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OPTIMIZING COAGULATION-ADSORPTION FOR
HALOFORM AND TOC REDUCTION

by

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16. ABSTRACT This study examines the removal of organic matter from Mississippi River water by coagulation and softening processes and identifies the influence of operating parameters upon the removal process. Furthermore, since activated carbon is typically employed to reduce organic concentrations, the effectiveness of various pretreatments were evaluated for their impact upon carbon bed life and the product water quality. Mainature carbon columns were used to evaluate the impact of various pretreatment strategies on the life and performance of carbon for organics reduction. Assessments were made of (1) removal of specific trace organics from the river water by coagulation, (2) effectiveness of various coagulants, coagulant aids, and lime softening in reducing the organic contents of river water, (3) the nature of the organics removed by coagulation and softening, (4) the effects of these processes on the behavior of miniature carbon columns, and (5) characterization of the organics removed by polarity and molecular weight fractionation studies. It was found that pH was the most important operating parameter. For example, reducing the pH to 5.0 improved organics removals in both coagulation and activated carbon adsorption. The service life of carbon was extended by up to 400% by comparison with similar studies conducted at pH 8.0. pH was also important in softening, and organics removal improved as the excess lime dose increased.		
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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

It has become evident that the organic content of source waters may react with drinking water disinfectants to form potentially toxic products. This problem may be minimized by reducing the organic precursor content of the water to low levels prior to disinfection. This report describes the results of a study to identify how activated carbon may best be used in conjunction with conventional coagulation and lime-softening treatment processes. The study highlights the important operating parameters that influence organics removal and also demonstrates the concept of optimum pretreatment for cost effective organics reduction.

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ABSTRACT

The natural organic content of surface and ground waters does not itself pose a significant public health concern. However, when these waters are chlorinated for disinfection, toxic chlorinated organics may be generated that pose a health threat to the consuming public. As a result there is a growing need to identify ways in which conventional water treatment plants may modify existing processes to improve the removal of these organics prior to chlorination.

This study examines the removal of organic matter from Mississippi River water by coagulation and softening processes and identifies the influence of operating parameters upon the removal process. Furthermore, since activated carbon is typically employed to reduce organic concentrations, the effectiveness of various pretreatments were evaluated for their impact upon carbon bed life and the product water quality.

It was found that pH was a most important operating parameter. For example, reducing the pH to 5.0 improved organics removals in both coagulation and activated carbon adsorption. The service life of carbon was extended by up to 400% by comparison with similar studies conducted at pH 8.0. pH was also important in softening, and organics removal improved as the excess lime dose increased.

Pretreatment was found to remove the higher molecular weight organic compounds most effectively and it was always observed that as the degree of pretreatment increased, the carbon service life was extended. Coagulation was found to provide better pretreatment than softening processes for Mississippi River water.

The data obtained provided the basis for a simple cost analysis and it was shown that an optimum level of pretreatment exists for a given overall water quality objective.

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SECTION 1

INTRODUCTION

- The organic content of water is troublesome for a number of reasons.
- (1) The organic content of natural waters is largely responsible for problems associated with color.
 - (2) Certain organic compounds contribute to taste and odor problems in drinking water supplies.
 - (3) The presence of organic compounds in treated water may foster problems associated with biological quality changes in the distribution systems (1).
 - (4) The presence of organic compounds in drinking water has been reported to aggravate corrosion problems in the distribution system (1).
 - (5) The presence of organic compounds may interfere in demineralization processes by fouling anion exchange resins and/or membranes (2,3).
 - (6) Organic compounds in water have been shown to interfere with the oxidation and removal of iron and manganese (5).
 - (7) Haloforms and other halogenated organic compounds can be formed when chlorine is added to water at the levels required for disinfection. The chlorine may react with both natural humic substances as well as certain anthropogenic compounds (6,7,8).
 - (8) Certain organic compounds are known to be toxic or carcinogenic and these may be harmful even at the very low concentrations at which they are present in water supplies. While humic substances themselves are thought to be harmless, these compounds may also have other materials associated with them such as pesticides, phthalates, and heavy metals (9,10).

The growing concern for the organic content of natural waters and their public health significance has highlighted the need for improved purification procedures. In February, 1978 the E.P.A. proposed that activated carbon be required in all water treatment plants serving 75,000 or more consumers in designated high risk areas (10). The standards of 100 µg/L for total trihalomethanes and 0.5 µg/L for each low molecular weight chlorinated organic compound were proposed for finished drinking waters. The THM regulation is now in effect for all utilities serving 10,000 or more customers. The GAC requirement was subsequently dropped, as was the proposed limit on each specific organic compound.

Recognizing these goals of minimizing the organic content of drinking water as a treatment objective requires that we re-evaluate the control process for existing treatment processes. Processes that have been fine-tuned for particulate removal, for example, may not be operating efficiently for the removal of the water's organic content.

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Coagulation is traditionally considered a pretreatment process for particulates removal. However, the process is instrumental in reducing the organic content of treated waters. If activated carbon must be used to reduce the organic content of the product water to an acceptable level, the pretreatment processes become extremely important. Activated carbon is an expensive unit process and if the coagulation process can be optimized for organics removal, then the reduced load to the carbon column will extend the expected life of the carbon while improving the product water quality and reducing the cost of treatment.

In October 1979 the Coagulation Committee of the American Water Works Association published a committee report concerning the removal of organics from water by the coagulation process (11). The report provided a very complete review of the literature and identified the needed research in this area.

Among the research needs highlighted were:

1. More fundamental studies for characterizing the removal behavior of the "real organic content of surface waters" rather than isolated humic or fulvic acids.
2. The utility of polymers as coagulant aids for organic removal needs to be better identified.
3. The character of organic compounds removed by coagulation needs to be identified.
4. A re-evaluation of the coagulation process as a pretreatment process for both turbidity and organic removal.

The studies and results reported in this report respond to some of these needs and hopefully provide answers and useful information to engineers and operators concerned with the most economical provision of a high quality potable water supply.

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CONCLUSIONS

For convenience, the conclusions are divided into sections. Each section presents a summary of the major findings and observations made in the results section of the report.

SPECIFIC TRACE ORGANIC REMOVAL FROM MISSISSIPPI RIVER WATER BY COAGULATION

Four C_{14} labelled model compounds were studied: phenol, benzoic acid, salicylic acid and octanoic acid. These compounds were used to spike river water samples so that removal studies could be conducted to test the effectiveness of coagulation in reducing their concentration. Alum and ferric sulphate were tested as primary coagulants and a study was conducted to identify the value of a cationic polymer (Purifloc C31) when used as a coagulant aid. All studies were conducted on the same river water sample so that the relative effectiveness of different conditions of operation could be tested.

Alum and ferric sulphate were found to be equally effective as coagulants on a weight basis for the reduction of total organic carbon (TOC) in river water and the optimum pH for these coagulants was approximately 5.0 and 4.0, respectively. The addition of a polymer enhanced coagulation for TOC and turbidity removal and it also eliminated the pH dependence of turbidity removal such that good turbidity removal was accomplished over the pH range from 4 to 9. Most benefit was gained from a 1 mg/L polymer dose. As polymer doses were raised to 5 mg/L, the benefit of the added polymer diminished. It was also noted that the polymer improved the performance of coagulation more when the primary coagulant was ferric sulphate.

The removal of the model organic compounds (100 $\mu\text{g/L}$ initial concentration) was relatively poor and in most cases, the extent of removal did not show a strong dependence upon coagulant dose. Removals of test compounds were typically <10% except for salicylic acid which was slightly better removed at higher alum dosages.

Studies on a synthetic river water with no organic content indicated that in the absence of naturally occurring organic matter, the removal of the trace organics was improved.

The influence of pH on trace organic removal provided an interesting result. Benzoic acid and octanoic acid showed either a very slight or no pH dependence, whereas phenol and salicylic acid were removed best in the pH range of 5 to 7.

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The mechanism of organics removal by coagulation is discussed based upon these results and it is concluded that complex formation may account for much of the observed removal behavior.

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A molecular weight fractionation study indicated that coagulation removed the higher molecular weight fractions of the naturally occurring organic organic matter. Low nominal molecular weight (less than 100 mmw) organics were only reduced by 10 to 20% even at high coagulant dosages.

COAGULATION STUDIES

A variety of coagulation studies were conducted on a single water sample to evaluate the relative effectiveness of organics removal under different operating conditions. The water sample tested was freeze concentrated and re-constituted to ensure a constant water quality during the study period. The use of various coagulants and coagulant aids was studied.

Polymers were studied in detail as primary coagulants and as coagulant aids. However, polymers were found to be relatively ineffective coagulants when used alone and they were more effective when used in conjunction with alum or ferric sulphate. Polymer addition was most beneficial when used with low doses of coagulant and improved the performance of ferric sulphate more than that of alum.

Polymeric charge and structure were evaluated. It was found that the cationic polymers tested were superior to anionic and non-ionic polymers which caused little or no improvement in organics removal during coagulation. Several different cationic polymers, selected for their differences in chemical structure and molecular weight, were tested. It was found that the improvements in organics removal caused by the use of these polymers were very similar. However, a slight improvement in organics removal was noted with increasing molecular weight and increased charge density.

The order of polymer/coagulant addition was not found to influence organics removal performance significantly. The slow addition of polymer was found to result in slightly better performance than a single one-shot addition of polymer of equal dose.

Activated silica was tested as a coagulant aid in conjunction with 20 mg/L alum and provided no benefit at pH 5.0.

Sequential coagulation studies were conducted at pH 5, 7 and 9. A marginal benefit was observed for multi-stage coagulation at higher pH values. However, the extra capital costs required to implement the process would outweigh the benefit gained in improved organics removal.

Organics removal by alum was found to be a largely reversible process. Coagulant added at pH 9 may remove more organics if the pH is later adjusted towards 5. Conversely, a coagulant employed at low pH may release organics back to solution if the pH is raised.

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SOFTENING STUDIES

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Softening studies were conducted to identify the impact of operating conditions on the effectiveness of organics removal from Mississippi River water. In addition, hardness removals were documented and the relationships between hardness removal objectives and organics removal were identified. The following may be drawn from this study.

The extent of organics removal and hardness removal were not influenced by the way in which the lime was added. Lime added as a dry powder gave the same performance as a lime slurry addition.

The rate of organics removal was quite rapid and over 95% of the observed removal was complete within 30 minutes. The CaCO_3 precipitated during recarbonation did not contribute to organics removal.

Alum addition with the lime improved the removals of both hardness and organics, but if too much alum was added, the resulting drop in pH caused a deterioration in performance. The order of alum and lime addition was found to be unimportant.

The use of a cationic polymer ARCO 6320P was tested in conjunction with alum. The results indicated that the polymer caused a slight deterioration in performance for both hardness and organics removal. The extent of organics removal during softening was found to be most strongly influenced by the operating pH. Softening at high pH gave better organics removal.

The primary mechanism of organics removal appears to be precipitation of the organics as calcium and magnesium complexes at high pH. Evidence is provided that suggests adsorption of organics to a $\text{Mg}(\text{OH})_2$ precipitate is not a major mechanism.

ORGANICS CHARACTERIZATION STUDY

A single large water sample was collected from the Mississippi River and subjected to various treatments prior to application to carbon columns. The pretreatments included alum coagulation, iron and polymer coagulation, and lime softening. Water samples were taken of the raw river water, following pretreatment, and following carbon adsorption. The samples were analyzed to determine the character of organics removed by each of the processes.

The organic content of each sample was fractionated according to molecular weight and polarity (33). Forty percent of the organic content of the river water was characterized as hydrophobic and 60% hydrophilic. The hydrophobic fraction was predominantly acidic, whereas the hydrophilic fraction was largely neutral in character. The molecular weight distribution of the river water for the fractions <1K, 1 to 10K, 10 to 100K and >100K was 23%, 50%, 10% and 17%, respectively.

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Coagulation with either alum or with iron and polymer gave similar performance. Hydrophilic acids were completely removed and hydrophobic acids

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were reduced by approximately 60%. The neutral fractions were also reduced. Lime by comparison was not as effective in removing the acidic fractions.

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Following GAC treatment where the pH was adjusted to favor adsorption, the organic content of the water was essentially independent of the pretreatment provided. Pretreatment reduced the higher molecular weight fractions most effectively and did not reduce the <1K fraction. Indeed, lime addition was observed to increase the concentration of organics <1K. GAC completely removed the remaining organics in the 1 to 10K fraction and ~ 60% of the <1K material.

Trihalomethane (THM) precursors were found to be associated with the acidic and neutral fractions with a molecular weight <10K. The removal of precursors of different character was also examined and it bore a strong correlation with the distribution of TOC.

A fingerprint of low molecular weight volatile organic compounds was made for each water sample tested following a technique developed by Suffet et al. (56), but no distinctive fingerprints were obtained. The results show little difference in character for waters receiving different pretreatments and the analytical methods used were probably not capable of determining the actual character of the various samples.

ACTIVATED CARBON COLUMN PERFORMANCE STUDIES

Through the use of miniature carbon columns containing between 3 and 7 mL of 50x80 mesh granular activated carbon (Westvaco WV-G) breakthrough curves were obtained for TOC, ultraviolet absorption (UVA) and THM precursors in 10-30 days. By different pretreatment conditions on the same water sample, the influence of pretreatment on carbon adsorption was identified. In some studies, synthetic resins were compared to activated carbon for pretreated river water. The following conclusions may be drawn:

(1) The removals of UVA, TOC and THM precursors by activated carbon all followed the same trends. The relationship between these parameters varied somewhat with different levels of treatment, but each parameter showed the same trends in all the studies. Thus, a pretreatment that was best for UVA removal was also the best for TOC and THM precursor removal. This suggests that simple analysis of UVA removal could be used as an indicator of the relative removal of TOC and THM precursors once a detailed correlation is established.

(2) The removal performance of activated carbon is strongly influenced by both solution pH and coagulant dose.

Effective carbon adsorption capacity was observed to improve as the pH was reduced. At pH 5, the capacity was approximately 3 to 4 times greater than that at pH 8 if column operation were terminated at 1 mg/L effluent TOC. If no coagulation were provided, the carbon was unable to reduce the TOC of the raw river water to an acceptable level and high TOC values broke through

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immediately. However, when coagulation was employed as a pretreatment, the organic content of the river water was significantly reduced and the carbon columns were able to produce an effluent containing very low concentrations of TOC. In addition, it was observed that carbon service life increased with increasing coagulant doses since higher doses caused a greater reduction in the influent organic concentration.

(3) The concept of an optimum pH value and coagulant dose was identified for pretreating Mississippi River water prior to the use of GAC.

(4) Lime softening was found to improve the carbon adsorption capacity for organics removal from Mississippi River water. Like the coagulation studies, it was found that increased levels of organic removal in pretreatment lead to longer carbon service life. In this regard, carbon adsorption capacities were observed to increase with increasing lime dose in pretreatment provided the pH was lowered for adsorption.

(5) For Mississippi River water, lime softening was a much less effective pretreatment process for organics removal than coagulation. The data obtained indicate that lime softening with 130 mg/L of high calcium quicklime and 7 mg/L of alum (as practiced at the Minneapolis Water Treatment Plant) was roughly comparable to pretreatment with 20 mg/L of alum at pH 5, in terms of organics removal effectiveness. A coagulant dose of 80 mg/L of alum gave far superior removal performance and extended GAC column life.

(6) Two weakly basic resins in the free base form were found to be inferior to activated carbon for adsorption of TOC and THM precursors from coagulated river water. These studies were conducted at pH 7, however, and the resins' performance may be improved by operating at different pH values.

(7) A column of strongly basic anion exchange resin, IRA 904 (in the chloride form) was found to be as effective as activated carbon for both TOC and THM precursor removal from coagulated river water samples.

The resin was also regenerated effectively with sodium chloride but further studies are needed to identify the best regeneration conditions for this resin.

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EXPERIMENTAL METHODS

WATER SOURCE

The water employed in this study was extracted from the Mississippi River close to the extraction point of the Minneapolis Water Treatment Plant. The Mississippi River arises from a peaty-swampy area in northern Minnesota and as a result is highly colored and rich in natural organic content. The concentration of synthetic compounds in the river water at this point is minimal since there are only about 100 discharges to the river above Minneapolis and the majority of these have very small flows.

River water samples were collected in 5 gallon glass carboys and then rough filtered by pumping (FMI Model RRP - Stainless Steel/Ceramic Head) downflow through 3 feet of filter sand (Neptune-Microfloc MS-6 Sand). The sand was supported in a 4-inch diameter glass column by 5 inches of graded gravel on a specially constructed glass diffuser plate. All tubing and connections were made of teflon. The filter effluent was pumped directly into a 55 gallon refrigerated stainless steel tank. When approximately 50 gallons of filtered water had been pumped into the tank, the refrigeration system was turned on. The contents of the tank were mixed with a stainless steel impeller and were frozen from the outside in. This concentration technique was developed by Shapiro (12,13) and in approximately 32 hours the concentrate with 90-95% of the original organic content of the river water (14) was reduced to about 7.5 gallons. This concentrate was removed and stored at 4° C in a stainless steel drum. Samples of the concentrate were later used to reconstitute river water of constant quality by simply adding organic free distilled water in the correct proportion.

In some studies river water samples were collected and stored at 4°C after filtration, without being concentrated. It was found that calcium carbonate/sulfates were precipitating from the concentrate following long storage periods. Although no significant change in organic content or character (as measured by removal behavior) occurred in the concentrates, it was decided that unconcentrated samples should be tested also. Tests were conducted as rapidly as possible to minimize the storage time.

COAGULATION TESTS

Reconstituted and normal river water samples were treated following a modified Jar Test technique (14). A Gang Stirrer (Phipps and Bird, Richmond, VA) was employed for flocculation; however, the rapid mix was provided by a

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separate high speed stirrer equipped with a teflon propeller. The desired volumes of coagulant and polymer stock solutions were injected into the vortex created by the rapid mixer and mixed for 5 to 10 seconds. The speed of rotation was then reduced to 30 rpm and acid or base addition (1N H_2SO_4 , 1N NaOH) was provided to adjust the pH to the desired value.

Following 30 mins. of flocculation at 30 rpm the samples were settled briefly and filtered through prewashed Whatman No. 1 filter paper. The filtrate was saved for analyses at 4°C. When turbidity measurements were required, 1 hour of sedimentation was provided prior to filtration. Sedimentation time did not influence organics removal. Earlier studies had indicated that the Whatman #1 filter paper simulated typical rapid sand filtration at 2 gpm/ft². Effluent water samples from a 3 ft. deep rapid sand filter and from the Whatman #1 paper contained identical concentrations of organics as measured by UVA and TOC.

The coagulants used were Fisher analytical grade aluminum sulfate ($Al_2(SO_4)_3 \cdot 18 H_2O$) and Mallinckrodt analytical grade ferric sulfate ($Fe_2(SO_4)_3 \cdot x H_2O$). Throughout the body of this text these coagulants are referred to as alum and iron. Stock solutions were prepared by dissolving 25 grams of alum or iron into 500 mls organic-free deionized water making a 50 g/L solution. The required amount of this stock solution was injected during the rapid mix using a Pipetman model P1000D adjustable pipette.

The procedures for preparation of polymer stock solutions were as recommended by the manufacturer. Generally, polymer doses were administered from a .05% polymer stock solution prepared with organic-free deionized water.

CARBON ADSORPTION STUDIES

Pretreatment-Coagulation

100 liter volumes of river water or reconstituted river water were transferred to a 40 gallon stainless steel tank. The contents of the tank were rapid mixed using a 1/4 HP direct drive motor and stainless steel impeller. The power input was controlled by coupling the stirrer to a Variable Auto Transformer (Staco-2PF 1010). The rapid mixer was mounted off center and turned up to create a vortex. The appropriate coagulant dose was added by pouring a known volume of stock solution (50 grams of either $Al_2(SO_4)_3 \cdot 18 H_2O$ per liter or $Fe_2(SO_4)_3 \cdot x H_2O$ per liter) into the vortex. Following 10 seconds of additional rapid mixing, the mixer was removed and replaced with a flocculator. The flocculator consisted of a 1/8 HP high-speed (500 rpm max) drive motor coupled to stainless steel flocculator paddles through a 20/1 reduction gear. The speed of rotation could be controlled using the variable transformer described above. The stirrer was equipped with three 12" x 1.5" stainless steel paddles. The top of the stainless shaft was tapped into 5/8" plexiglas rod to insulate the contents of the flocculator. This was designed to avoid electrical interference created by the motor from affecting the measurement of solution pH.

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Right after rapid mixing the pH was adjusted and maintained at a given value by means of a Leeds and Northrup Model 7075-3 pH Controller and Electrode Transmitter which had been modified to receive laboratory pH probes. This on-off controller operated 2 Asc0 1/16" stainless steel solenoid valves for the controlled addition of acid and base. The contents were flocculated for 30 minutes at a speed of 10-30 rpm.

Following flocculation the contents of the tank were allowed to settle for 1 hour. The settled water was pumped at 250 mL/min through a trimedia filter. The filter, contained in a 4-inch glass column, consisted of 9 inches of anthracite, 9 inches of sand, and 9 inches of garnet. The media were supported by four inches of graded gravel on a coarsely sieved glass disc. The first 3 liters of filtered water were discarded and the remainder was collected in covered 10 gallon stainless steel tanks. Following the filtration of each batch of water the filter was backwashed for 10 minutes at 50% expansion with tap water.

Pretreatment - Softening

The procedure for lime softening was very similar to that described above for coagulation. Lime (high calcium quicklime (CaO) analytical reagent grade - Sigma Chem) and coagulants, if used, were added simultaneously during the rapid mix which was extended for 30 seconds. The lime was added as a dry powder in most studies since it was demonstrated that no benefit was derived from slaking the lime prior to addition. Sedimentation following flocculation often required longer than 1 hour for good clarification, especially if a coagulant were not employed. Following sedimentation the water was filtered as for coagulation.

The solution pH was checked and adjusted daily, if necessary, by the addition of Na_2CO_3 or H_2SO_4 to the treated water.

Mini-column Operation

The filtered water was pumped (Gilson Mini-Puls II Model 42746-HP8) to the mini-columns of carbon. The mini-columns (Glenco 3400 series 0.9x30 cm) contained 6 to 9 cm of 50x80 Nuchar WV-G carbon supported on 2 cm of sand. Before contacting the carbon with treated water the carbon was backwashed with carbon-filtered distilled water to remove fines and stratify the bed; then treated water was pumped downflow through the carbon columns at a flowrate of 3-4 mLs/min. This loading rate was equivalent to 1.1-1.5 gpm/ft². Depending upon the carbon depth, the empty bed contact time ranged between 1.0 and 2.0 minutes.

The column effluent flowed into 100 mL glass collection chambers. The overflow from the collection chambers flowed directly to a drain. The contents of the collection chambers were sampled automatically once every 2 hours by a specially designed 72 bottle fraction collector. The samples were drawn by Masterflex pumps (Model 7545 with #7014 heads) through 1/8" teflon tubing. After a sample was taken, the pumps operated in reverse to purge the sampling lines of any residual liquid. Samples were collected in

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8 oz. cylindrical, clear, screw-cap bottles and stored at 4°C for analysis. Studies conducted over a 10-day period (or longer) were sampled manually twice a day.

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Flowrates to the columns were checked every 12 hours and adjustments in flowrate were made as necessary to ensure constant and equal flowrates to all the columns. If the headloss build-up in a column reduced the flowrate to an unacceptable level, it was taken out of service and backwashed with carbon-filtered distilled water. Extensive backwashing was avoided and the columns were returned to service as soon as the turbidity was flushed from the column.

Samples were adjusted to pH 4.0 with H_2SO_4 after collection and stored for analysis. For a column study all the analyses were conducted at the same time to avoid errors arising from instrumental variation from day to day and following separate calibration procedures. All UVA and TOC analyses were conducted with the samples at pH 4.0.

ANALYTICAL METHODS

- (1) Total Organic Carbon (TOC): TOC measurements were made using a Barnstead Photochem Organic Carbon Analyzer (Barnstead Co., Boston, MA). This instrument employs ultraviolet radiation to oxidize organic matter to carbon dioxide which is then measured by the increase in conductivity of a pure water reservoir maintained within the instrument. The instrument proved reliable and provided accurate, reproducible data in the range of 0.1 to 8 mg/L of TOC when the manufacturer's recommended techniques were followed.
- (2) Ultraviolet Absorbance (UVA): UVA was monitored using a Beckman Model 26 Ultraviolet-Visible Spectrophotometer (Beckman Instruments, Fullerton, CA). Absorbance was measured using a 5 cm quartz cell at 254 nm. All samples in any test run were brought to pH 4.0 with H_2SO_4 prior to UVA measurement.
- (3) Trihalomethane Measurement: Trihalomethane (THM) measurements were conducted using pentane extraction and gas chromatography (GC) using an electron capture detector (ECD).

Four mL of chlorinated water sample were extracted with 1 mL of "distilled in glass" n-pentane (Burdick & Jackson) in an 8 mL glass centrifuge tube fitted with a teflon-lined screw cap. The contents were shaken for 30 seconds and 3 μ L of the pentane was then injected into the GC. The GC used was a Hewlett Packard Model 4840A which was equipped with a 6 ft. x 1/8" column packed with 3% SP1000 on 100/200 Supelcoport (Supelco). The GC was programmed to hold the temperature at 60° for 1.5 minutes and then raise the temperature to 80°C with a temperature ramp of 20°C/minute. The run was terminated at 5.5 minutes. The carrier gas was hi-purity nitrogen and the flowrate was set at 25 mLs/min. Chloroform, dichlorobromomethane, dibromochloromethane and bromoform peaks were obtained on the chromatogram and the concen-

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trations of the individual trihalomethanes were identified by the calibrated integrating recorder.

The recorder/programmer of the GC unit was calibrated from known standards according to Hewlett Packard's recommended procedure. Known standards were prepared daily from a standard stock solution. The latter solution was prepared weekly in the following manner. A 10 mL volumetric flask was filled with about 9.5 mLs of Omni-Solve grade methanol (MCB Reagents, Cincinnati, Ohio). The flask was then placed on a Mettler Model A30 top-loading analytical balance and one or two drops of chloroform were then added and the net weight change was recorded. The other trihalomethanes were added in the same fashion. The flask was then brought up to volume with additional methanol and stored at 4°C.

Knowing the weight concentrations of the chlorinated compounds in the stock solution, standard solutions for calibration of the GC were prepared by dilution. Microliter syringes (Hamilton Co., Reno, Nevada) were used to measure 50 to 150 μ L of stock solution into 50 to 150 mLs of carbon treated distilled water. These standard solutions were prepared each day THM analyses were to be conducted.

In this study total trihalomethane formation potential (TTHMFP) was measured by measuring the THM concentrations in samples of water that were chlorinated. 8 mL of the water sample to be chlorinated was transferred to a clean 8 mL centrifuge tube. The sample was then chlorinated by a subsurface addition of 152 μ L of 4% solution of Hi-Lex Bleach (Pirex Corp., Lakewood, CA) in carbon treated distilled water. This left a small head space that was filled with 2 drops of saturated sodium bicarbonate to buffer the pH at 8.0. The samples were then capped with teflon-lined screw caps, shaken and inverted and stored at room temperature for 48 hours. At the end of the chlorination period the residual chlorine was quenched by the addition of 2 drops of sodium thiosulfate. Four mL of the chlorinated sample were withdrawn from the tube using a volumetric pipet. The remaining contents of the tube were then emptied and the 4 mL were returned to the tube. The chlorinated sample was then extracted following the procedure described above.

The addition of bleach provided an equivalent dosage of chlorine of 28 mg/L and earlier studies by Semmens had identified that under these conditions of chlorination the THM concentrations obtained were relatively insensitive to small changes in chlorination time and chlorine dose. The procedure was therefore good for identifying changes in TTHMFP resulting from different treatment methods.

- (4) Turbidity: Turbidity was measured using a Hach Model 2100A Turbiditymeter (Hach Chemical Co., Ames, IA).
- (5) Scintillation Counting: All scintillation counting was performed on a Beckman Mark II Scintillation Counter. The actual counts per minute (cpm) were sufficiently high so that each sample was counted for four minutes.

Counting efficiencies were reported as the ratio of the counts of an external standard registered by the two channels. These ratios were converted to percentages by utilizing a calibration curve prepared from known standards in quenched samples of the dioxane scintillation liquid. The actual disintegrations per minute were determined by dividing the counts per minute by the efficiency. A dioxane-based scintillation liquid was made with 500 mLs p-dioxane, 3.5 g 2,5-diphenyl-oxazole, 0.25 g 1,4-bis [2-(5-phenyloxazoly)] benzene, and 500 g naphthalene.

Two mL of each sample to be analyzed were pipetted into a glass scintillation vial. Ten mLs of the scintillation liquid described above were added to each vial and the vial was sealed with a teflon-lined cap. These samples were stored at 4°C until they were placed into the counter for analysis. Normally twenty to thirty samples were counted per run and samples were always counted within one week after the addition of the scintillation liquid to minimize the chance of error due to loss of scintillation liquid by evaporation.

The reproducibility of the scintillation analyses was checked by repeating a coagulation test for each of the four organic compounds listed in Table 1 four times. The percent removals for each of the compounds were determined for 200 mg/L of alum at pH 5 for the four tests. Mean values and standard deviations for these tests are shown in Table 1.

TABLE 1. REPRODUCIBILITY OF SCINTILLATION ANALYSES FOR PERCENT REMOVAL

Compound	$\bar{x}$	σ
Benzoic Acid	4.2	1.4
Octanoic Acid	3.4	1.8
Salicylic Acid	18.8	2.5
Phenol	2.3	1.6

- (6) Molecular Weight Fractionation (MWF): River water and variously treated water samples were fractionated into four molecular weight ranges by ultrafiltration. Millipore PT Series 90 mm membranes (Millipore Corp., Redford, MA) with nominal molecular weight limits (nmwl) of 1,000, 10,000 and 100,000 (1K, 10K, 100K) were used. The fractionation technique utilized was previously described by Eisenreich, et al. (30).

Prior to the initiation of the fractionation study, the membranes were preconditioned by allowing them to soak in Photochem water*

*Water taken from the Barnstead Photochem TOC Analyzer.

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(Millipore). Photochem water was passed through the membranes until the TOC content of the effluent water was less than .05 mg/L (usually about 2L). The filters were then conditioned with the sample to be fractionated. 500 mL of sample at pH 4.0 was placed in the filtering apparatus and the reservoir was pressurized (15 psig for the 100K and 10K membranes and 40 psig for the 1K membranes). The sample was filtered until 30% of the sample (150 mL) remained in the reservoir. Both the permeate (the filtrate) and retentate (the unfiltered fraction) were discarded. Following this conditioning procedure, 3.5 liters of the sample at pH 4.0 were filtered. The ultrafiltration cells utilized were able to accommodate only 500 mL portions of the water at one time. Five hundred mLs were placed in the ultrafiltration cell containing the 100,000 nmwl membrane and pressure was applied. After 350 mLs had passed through the membrane, the pressure was released and the retentate and permeate were saved. This procedure was repeated seven times to treat the entire sample and the retentates and permeates were blended prior to analysis.

The actual fractionation scheme is delineated in Figure 1. A water sample to be fractionated was first applied to the 100,000 nominal molecular weight limit (nmwl) membrane. The permeate from the 100K membrane was then applied to the 10,000 nmwl membrane in the same fashion, and the permeate from this membrane was in turn applied to the 1,000 nmwl membrane as depicted in Figure 1. One hundred mL samples of the retentates, the permeates and the original water were placed in glass bottles capped with aluminum foil and stored at 4°C until analyzed.

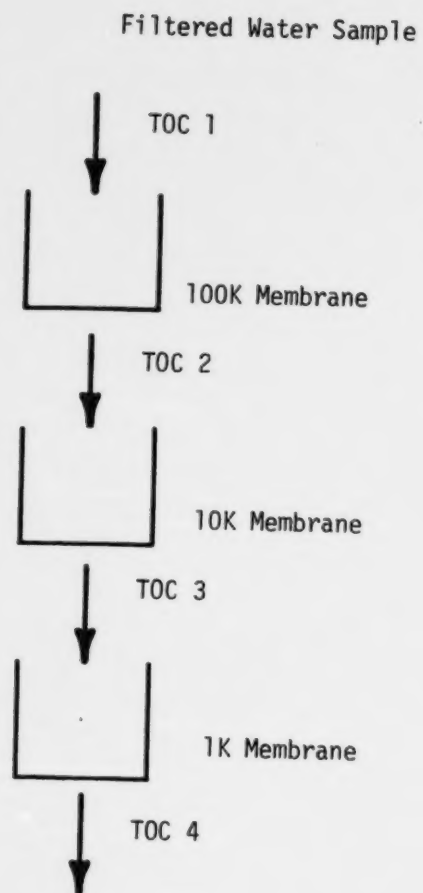
Computation of molecular weight fractions was readily conducted by a mass balance approach. The approach assumes that the measured organic concentration of the permeates represents the concentration of compounds having molecular weights below the specified membrane size. This is a simplistic assumption since many factors influence membrane rejection efficiency (15,31) such as pH, pressure applied, degree of concentration and structural character of compounds. However, accepting this assumption and recognizing the operational nature of the fractionation procedure the molecular weight fractions may be calculated as shown below in Table 2. The TOC sample abbreviations correspond to the samples shown in Figure 1.

TABLE 2. COMPUTATION OF MOLECULAR WEIGHT FRACTIONS

<u>Fraction</u>	<u>Determination</u>
Greater than 100K	TOC1 - TOC2
10K - 100K	TOC2 - TOC3
1K - 10K	TOC3 - TOC4
Less than 1K	TOC4

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Ultrafiltration terminated when the permeate volume was equal to 70% of the applied sample volume.

Figure 1. Schematic representation of the molecular weight fractionation procedure.

(7) Polarity Fractionation (PF): Polarity fractionation is a fractionation scheme which separates organics having different sorptive character. The technique is essentially the same as that first described by Leenheer and Huffman (33).

Three glass and teflon columns were prepared. The first column measured 0.9 cm x 30 cm and contained 7.5 mLs of XAD 8 resin packed over 7.5 mLs of XAD 2 resin. Both resins were provided by the Rohm and Haas Co., Philadelphia, PA. The second and third columns measured 0.6 x 30 cm and contained 21.5 cm of cation exchange (AG-MP 1) resins and anion exchange resin (AG-MP 30), respectively. Both exchange resins were provided by BioRad, California.

All the resins were cleaned by successive soxhlet extractions with methanol, acetonitrile and ether for 24-28 hours with each solvent. The cleaned resins were stored under methanol. The ion exchange resins were also conditioned with treatments of 1N H₂SO₄ and 1N NaOH. The packed columns were eluted with 300 mL of 0.1N NaOH, 300 mL of 0.1N H₂SO₄ and then rinsed with Photochem water until the effluent TOC was less than 0.1 mg/L. Flowrates during the elution and cleaning procedures ranged between 1-3 mLs per minute. Immediately prior to use all three resin columns were flushed with 100 mL of Photochem water to ensure the displacement of organics that may have leached from the resins while the columns were idle.

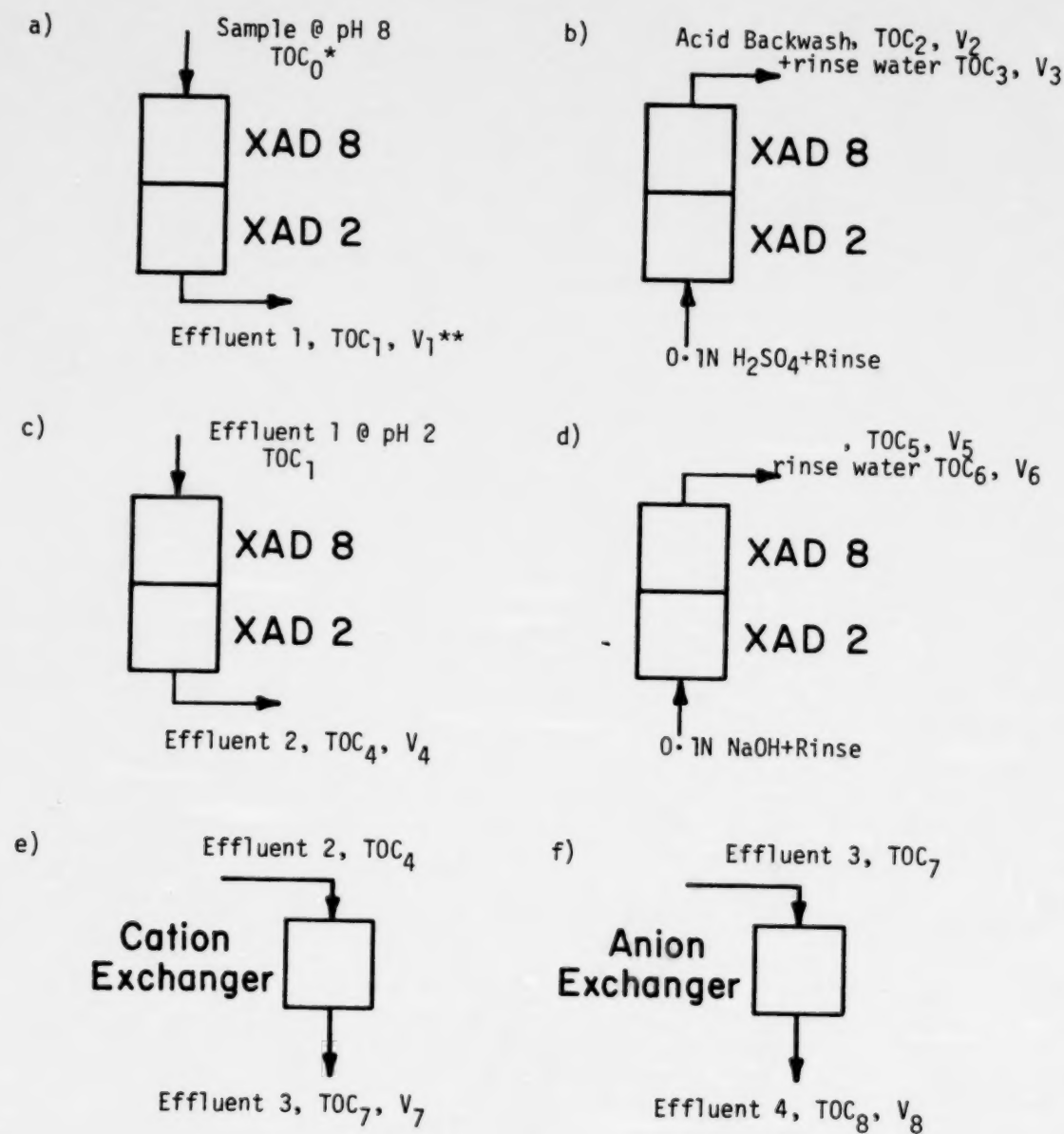
A 2-5 liter water sample to be fractionated was adjusted (if necessary) to pH 8.0-8.3, passed downflow through the XAD 8/2 column and the effluent was collected. The column was then backwashed with 100 mL of 0.1N H₂SO₄ and the acidic eluate was saved. The column was rinsed with 100 mL of Photochem water and the rinse water was also saved for analysis. The effluent sample was adjusted to pH 2 and repassed through the XAD 8/2 column downflow. The effluent from this stage was pumped downflow through the cation and anion exchange columns in that order. Samples of the effluents from each column were returned for analysis. The XAD 8/2 column was eluted upflow with 100 mL of 0.1N NaOH and the eluate was preserved for analysis.

The flowrates for samples and eluates applied to the columns were constant at 3-5 mL/min. The entire procedure is depicted schematically in Figure 2.

Following the fractionation of a water sample, the XAD 8/2 resin column was cleaned with 100 mL of methanol and rinsed with Photochem water (at a flowrate of approximately 3 mL/min) until the effluent TOC dropped to 0.1 mg/L.

The computation of the polarity fractions in a water sample were conducted as follows:

$$1) \text{ Hydrophobic bases} = H_B = \frac{V_2 \cdot \text{TOC}_2 + V_3 \cdot \text{TOC}_3}{V_1} \text{ mg/L}$$



* = Measured TOC of sample

** = Measured volume of sample

Figure 2. A schematic representation of the sequence of operations for polarity fractionation analysis.

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- 2) Hydrophobic acids = $H_A = \frac{V_5 \cdot \text{TOC}_5 + V_6 \cdot \text{TOC}_6}{V_4}$ mg/L
- 3) Hydrophobic neutrals = $\text{TOC}_0 - \text{TOC}_4 - H_A - H_B$ mg/L
- 4) Hydrophilic bases = $\text{TOC}_4 - \text{TOC}_7$ mg/L
- 5) Hydrophilic acids = $\text{TOC}_7 - \text{TOC}_8$ mg/L
- 6) Hydrophilic neutrals = TOC_8 mg/L

GC/FID Analysis

A 0.9 cm x 30 cm solvent resistant column constructed from glass and teflon (Glenco, Houston, TX) was packed with precleaned XAD 2 resin (50 x 80 mesh). The resin supplied by the Sigma Chemical Company was cleaned prior to use by successive soxhlet extraction for 24 hours each in methanol, acetonitrile and diethyl ether. The precleaned resin was added to the column to provide a bed depth of 18 cm and then flushed downflow with carbon-treated distilled water which was pumped to the column from a glass reservoir by means of a Gilson Minipuls II Model 42746-HP8 pump adjusted to provide a flowrate of 3.5 mL/min. The column was maintained under a slight positive head, to avoid air bubble formation in the resin bed. The head was provided by raising the effluent discharge level to a point several feet above the column. Any turbidity or suspended matter present in a sample was removed by a glass wool plug in the influent line to the column. The water was only exposed to teflon and glass except for the soft vinyl tubing used on the pump. Following an extensive flushing procedure with distilled water, the resin was ready for use.

The sample was pumped through the resin at 3.5 mL/min downflow at pH 8.3. The volume of sample extracted varied with the quality of the water. For example, 10 liters of river water were extracted, while for pretreated and carbon treated waters, 20 and 40 liters of water were extracted, respectively. After the sample had been pumped through the resin, the pump was disconnected from the feed line to the column and 100 mL of pesticide quality diethyl ether (Burdick and Jackson) was siphoned at 1 mL/min upflow through the resin column in 20 mL increments. Following the passage of each 20 mL volume of ether, the column was inverted several times and the resin was allowed to resettle. This procedure ensured uniform contact between the resin and ether. The ether extract was collected in a separatory funnel to which was added 2 grams of anhydrous soxhlet extracted (diethyl ether) Na_2SO_4 . The contents of the funnel were sealed and shaken vigorously.

The ether extract was separated and transferred to a Kurdurna Danish apparatus in which it was concentrated to approximately 3 mL. The cooled concentrate was then transferred to a Micro Snyder apparatus and further concentrated to 0.5 mL. The concentrate was stored in a 2 dram vial fitted with a teflon-lined seal and refrigerated to -10°C.

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Prior to "fingerprinting" extracts of any water samples, two fresh XAD 2

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columns were prepared and extracted with ether to provide a basis for comparison. The extracts were concentrated and analyzed by GC/FID under the conditions described below to identify if any compounds were being eluted from the resins by the ether. The chromatograms are referred to as blanks in this report since they reflect the background chromatogram attributable to the resins and ether alone. Furthermore, since there was a possibility that some organics may adsorb irreversibly to the XAD 2 resin such that the first exposure of the resin to river water might yield atypical results compared to subsequent studies, the resin was conditioned. For this step two 70 liter batches of filtered river water were collected. One batch was chlorinated (20 mg/L as Cl_2 by NaOCl addition) for 24 hours and quenched with sodium thiosulfate. The two batches were then combined and the solution was pumped to both resin columns at 3.5 mL/min. Following this, the resins were extracted with 100 mL of ether per the procedure described above. This ether extract was discarded. The resin columns were rinsed with an excess of distilled water and were ready for the first sample to be tested.

The extracts were analyzed using a Varian Model 2780. Gas Chromatograph (GC) fitted with a single flame ionization detector (FID). The best conditions for operation of the GC/FID were selected after extensive testing of flowrates, temperature programs and packings. The conditions reported by Suffet et al. (56) were tested first, but it was found that the recommended packing (20% SE 30 on 80/100 Gas Chrom Q) caused an unacceptable "Chromatogram" when the GC temperature program was initiated without a sample injection. The "chromatogram" was the result of extensive column bleed and the recommended packing was unacceptable for this study. Perhaps with dual FID's (56) the column effect may have been eliminated but for a single FID a relatively clean blank was essential. It was found that a 6 ft. x 14" column packed with 6% SE 30 on 80/100 Gas Chrom Q gave good peak resolution and an acceptable "blank chromatogram." The GC was temperature programmed to start at 50°C and rise at 10°C/min to a maximum of 200°C. A run was terminated after 45 minutes. Gas flowrates were adjusted to 300, 30 and 30 mL/min for air, hydrogen and nitrogen respectively. The injector and detector temperatures were set at 230 and 300°C, respectively.

Prior to use, the column packing was conditioned at 210°C for 48 hours. When ether blanks were injected to obtain a background chromatogram, it was apparent that a very large solvent peak was obtained. The chromatogram took up to 10 minutes to return to baseline and it was observed that the level of attenuation needed to be adjusted during the course of a run in order to keep the graph and its peaks well positioned on the paper. The character of the chromatograms obtained is more completely discussed in Section 6 of this report.

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SECTION 4

SPECIFIC TRACE ORGANIC REMOVAL
FROM MISSISSIPPI RIVER WATER BY COAGULATION

INTRODUCTION

Many studies have been conducted to evaluate the performance of coagulation with aluminum and ferric salts for reducing the concentration of color or humic substances in water (11). Humic substances range in molecular weight from a few hundred to tens of thousands (16,17) and are chemically complex polyelectrolytes having a negative surface charge in natural waters. The chemical character of the humic substances is still being studied; however, they are thought to be predominantly aromatic having varying quantities of carboxyl, phenolic, alcoholic, ketonic, quinoid and methoxyl functional groups that render them hydrophilic in nature. Because the size of these macromolecules approaches colloidal dimensions, humic substances are often classified as colloids even though they may be truly dissolved (18).

The removal of humic substances by coagulation may then be explained in terms of the various mechanisms of colloid destabilization and subsequent flocculation (15). However, smaller, truly dissolved organic compounds that may be present in surface water may also be removed during the coagulation process by mechanisms such as specific adsorption to floc particles and co-precipitation but very little research has been conducted in the area of soluble organics removal by coagulation.

Sridharan and Lee (19) studied the removals of phenol, citric acid, and glycine by co-precipitation with iron from waters of differing quality. Concentrations of iron in the range of 0.005 to 0.025 M FeCl_3 (280-1400 mg/L Fe) removed approximately 60 to 90% of the phenol, 20 to 25% of the glycine and 20 to 70% of citric acid in spiked water samples. Lower iron concentrations in the range of conventional coagulation practice were not studied. The percentage organic removal was apparently not as sensitive to iron dosage as it was to solution pH, type of compound considered, and the quality of the water studied. Earlier works include those of Tatsumoto *et al.* (20) who recovered 53% of C_{14} -labelled phenylalanine from seawater by co-precipitation with iron; Chapman and Rae (21) who obtained a recovery of 16 to 90% of various organic compounds from seawater with ferric hydroxide, and Williams and Zirino (22) who recovered 36 to 63% of the organic matter from seawater using ferric hydroxide.

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In all the above studies on soluble organics removal, the systems

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studied were extremely complex and few conclusions may be drawn from these results other than the observation that iron has the potential for reducing the soluble organic concentration of a water.

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In a more simple and controlled study Semmens and Ocanas (23) studied resorcinol and dihydroxybenzoic acid (DHBA) removal by iron from distilled water and 10^{-3} M NaHCO_3 solutions. Removals were influenced by coagulant dose, solution pH and organic concentration. However, up to 25% DHBA and 8% resorcinol removal were achieved with coagulant doses of approximately 3×10^{-4} M $\text{Fe}_2(\text{SO}_4)_3$ (120 mg/L). The behavior of simple model compounds was similar in many respects to the observed behavior of humic substance removal by coagulation (11) and studying the behavior of these compounds may provide insights into the mechanics of organic removal.

The present study was intended to investigate the removal behavior during coagulation of several selected model compounds from a natural surface water matrix. In this way the removal effectiveness of model compounds from river water could be compared and contrasted with the removal behavior of the natural organic content of the water.

Organic Compounds

Four organic compounds were selected for study. The compounds were selected for their similarity to structural components of the fulvic acid macromolecules (24) and are representative of the type of low molecular weight compounds that may be found in low concentrations in the breakdown of lignins, tannins and humic substances (25). Similarly, aromatic carboxylic acids are formed during the breakdown of humic substances and may be found in concentrations as high as the milligram per liter level (25). Aliphatic carboxylic acids have also been detected in Mississippi River water in significant concentrations (26,27).

It is also well known that polyhydric phenolic and substituted aromatic carboxylic acids are susceptible to oxidative rupture of the benzene ring during chlorination and these types of compounds must be considered as potential haloform precursors.

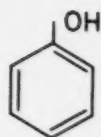
The compounds selected were phenol, benzoic acid, salicylic acid and octanoic acid and were purchased labeled with C_{14} . All of the compounds were similar in molecular weight as shown in Figure 3 and enabled comparisons to be made to identify the impact of functional groups on removal performance. Similarly, comparisons between aliphatic versus the aromatic character could be made by comparing octanoic acid versus benzoic acid.

Test Procedure

All of the labeled model compounds were added to a reconstituted river water sample at concentration of 100 ppb. The spiked river water sample was then subjected to coagulation studies following the jar test procedure. Following coagulation, the filtered water samples were analyzed for turbidity, TOC, UVA and trace organic concentrations by liquid scintillation counting.

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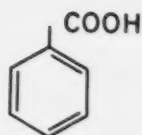
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PHENOL

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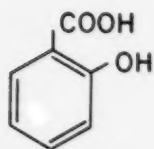
MW = 94



BENZOIC ACID

$pK = 4.19$

MW = 122

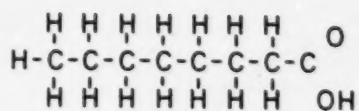


SALICYLIC ACID

$pK_1 = 2.97$

$pK_2 = 13.40$

MW = 138



OCTANOIC ACID

$pK = 4.89$

MW = 144

Figure 3. Structural configuration of the four model organic compounds examined.

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A synthetic river water sample was also constituted by adding inorganic salts to organic free, distilled water. The model compounds were added to this water sample and the pH was adjusted to that of the river water. Jar test studies conducted on the synthetic water were compared with those conducted on the river water to identify the impact of the natural organic content upon trace organic removal behavior.

Discussion of Results

Iron and aluminum sulphate salts were compared alone and in conjunction with Dow Purifloc C31 cationic polymer (See Section 5 and Figure 19) for their ability to remove turbidity and organics from Mississippi River water. The removal behavior of the natural organic content is reported first to characterize the water sample studied.

The first jar tests were conducted to evaluate the impact of coagulant dose. The results are shown in Figure 4. Dosages ranged up to 300 mg/L and it was apparent that ferric sulphate and alum were equally effective in removing organics on a weight basis. With both coagulants an approximately linear increase in organics removal was observed between 0 and 200 mg/L of coagulant added. The addition of greater coagulant dosages did not appear to increase organics removal significantly.

The slopes of the linear sections of the curves shown in Figure 4 are very similar. However, the curve obtained with iron had a slope that was 16% less than that obtained with alum. This difference is undoubtedly strongly influenced by the operating pH. As discussed below, iron and alum salts have different pH optima and the data presented in Figure 4 was collected at pH 5 which was the observed optimum pH for alum and not for iron.

The turbidity removals are also presented in Figure 4 for different coagulant doses. Alum was clearly superior to iron in removing turbidity at low coagulant doses. At concentrations above 100 mg/L of coagulant dose, both iron and alum showed little significant benefit in turbidity removal performance.

The influence of solution pH on coagulation performance was evaluated. The results are shown in Figure 5 for a coagulant dose of 50 mg/L. The data indicated that pH 5 and pH 4 gave the best organics removal for alum and iron coagulants, respectively. At this coagulant dose, the turbidity removal was best at high (>8) or low (<4) pH and there was no apparent relationship between the optimal pH for organics removal and that for turbidity removal. The influence of solution pH was also evaluated when a cationic polymer was employed as a coagulant aid. 5 mg/L of Purifloc C31 was added in conjunction with either an alum or an iron dose of 50 mg/L. The results are presented in Figures 6 and 7, respectively. It was apparent that the addition of polymer enhanced both turbidity and organics removal. However, while the pH effect on organics removal remained unchanged with a marked optimum at 5 for alum and 4 for iron, the pH effect on turbidity removal was virtually eliminated and turbidity removal was effective over the entire pH range studied.

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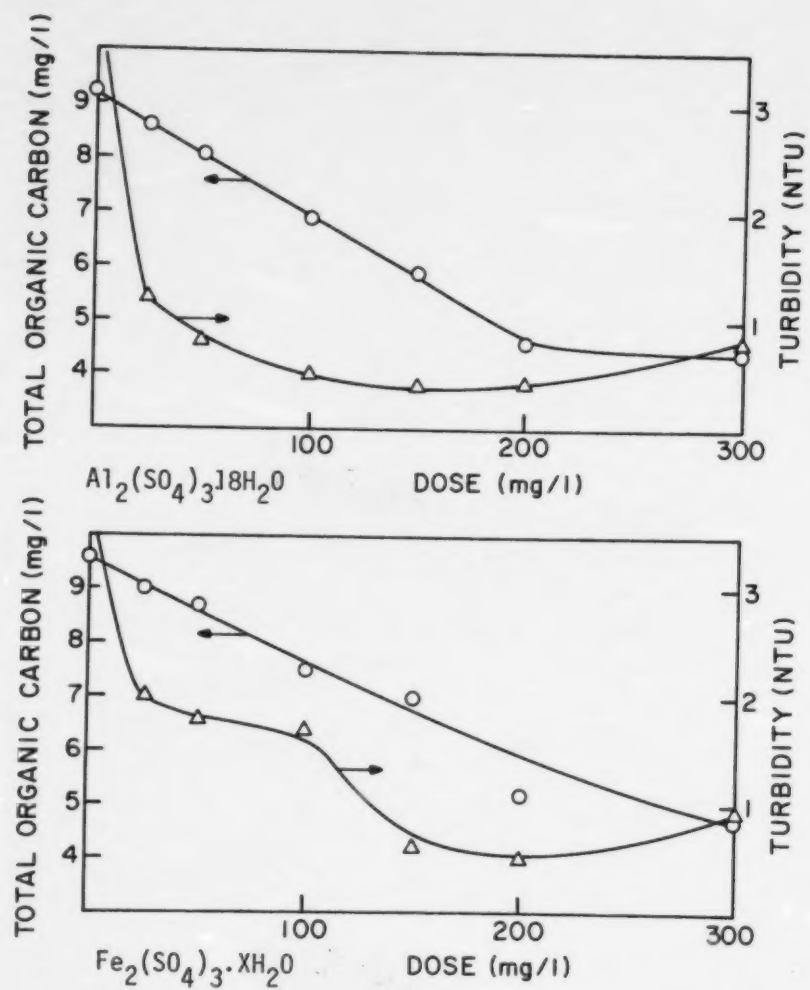


Figure 4. Dose effect for the removal of turbidity and TOC from Mississippi River water at pH 5.

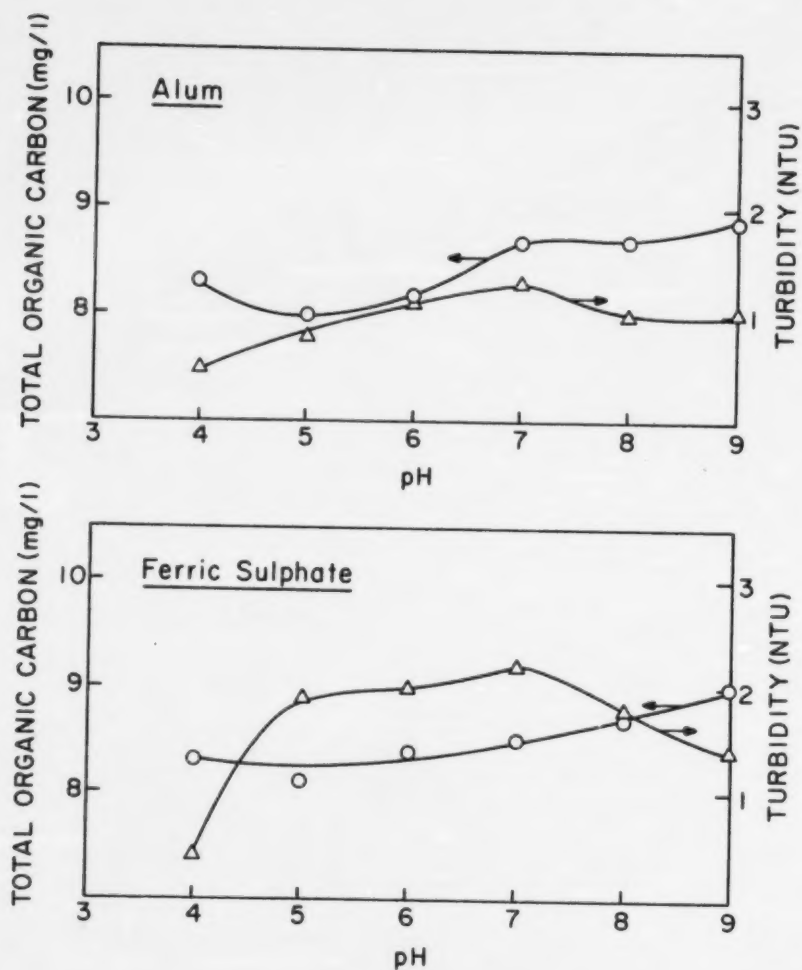


Figure 5. pH effect for the removal of turbidity and TOC from Mississippi River water coagulant dose = 50 mg/l.

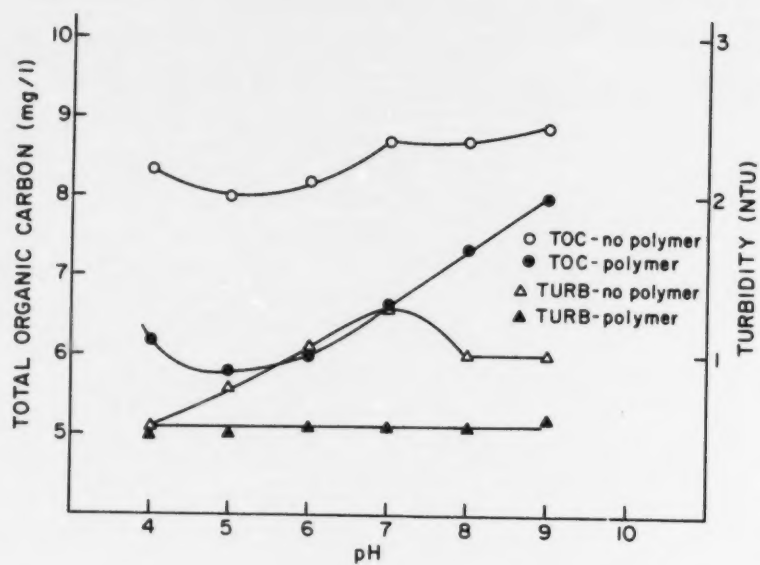


Figure 6. pH effect for the removal of turbidity and TOC from Mississippi River water with 50 mg/l alum and 5 mg/l Purifloc C31 polymer.

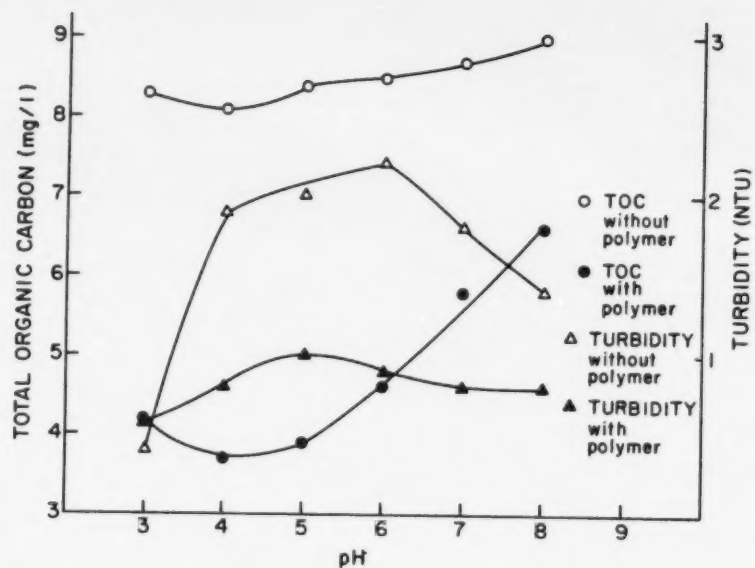


Figure 7. pH effect for the removal of turbidity and TOC from Mississippi River water with 50 mg/l $\text{Fe}_2(\text{SO}_4)_3$ and 5 mg/L Purifloc C31 polymer.

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The impact of polymer addition was evaluated at a variety of coagulant doses. The results are summarized in Figure 8. Polymer doses ranged between 1 and 5 mg/L and the metal coagulant salts were added in concentrations ranging between 25 and 100 mg/L. The addition of polymer generally improved TOC removal. Most benefit was gained from the addition of 1 mg/L of polymer; higher polymer dosages did not improve organics removal markedly. The iron coagulant appeared to benefit more from the addition of polymer than did alum. With the addition of 1 mg/L of polymer, an increase in TOC removal of approximately 40% was gained in conjunction with 50 mg/L of iron, whereas only a 10% improvement was noted with a corresponding alum dose.

With alum the addition of polymer did not significantly alter the turbidity removal performance; however, with iron as a coagulant the polymer improved performance. For iron, turbidity removals increased as the polymer dose was increased to 3 mg/L and no benefit was derived from higher coagulant doses.

Figure 8 and the observed turbidity removal behavior indicate that both turbidity and organics removal must be monitored for varying coagulant doses and polymer doses if the optimum conditions are to be identified for pretreatment.

Trace Organic Results

The influence of coagulant dose is shown in Figures 9 to 12. The impact of coagulant dose was evaluated at pH 5 in both Mississippi River water and Milli-Q water to which inorganic salts had been added so that it had the same inorganic composition as the river water. In this way the impact of the organic content of the river water on removal behavior could be identified.

Examination of Figures 9-12 indicates that generally the model compounds were poorly removed by coagulation and that in most cases the extent of removal did not show a strong dependence upon coagulant dose. The behavior of salicylic acid removal (Figure 11) proved an exception and showed a significant increase in percent removal at an alum dose of 200 mg/L.

As noted above in the analytical section, the % removals were generally reproducible with a standard deviation of approximately 1.5-2%. So the increase observed for salicylic acid was significant.

Comparison of the observed behavior in Milli-Q water and actual river water indicated that when natural organics were not present, better removals of the model organic compounds were generally observed. In the case of octanoic and salicylic acid the difference was very pronounced as shown in Figures 9 and 11. For phenol, a small but significant improvement was noted but benzoic acid showed almost identical removal behavior in both waters.

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The impact of solution pH is documented in Figures 13-16. Interestingly, benzoic acid and octanoic acid showed very slight or no pH dependence

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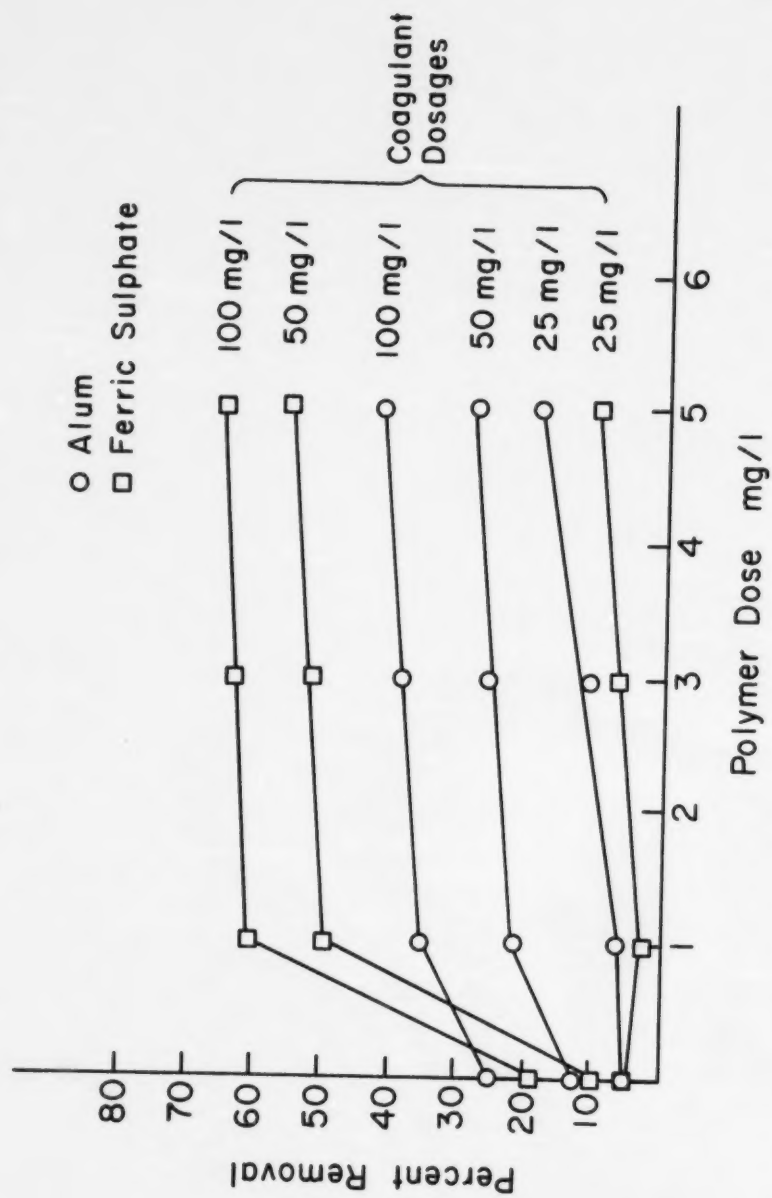


Figure 8. Effect of polymer dose (Purifloc C31) on removal of TOC from Mississippi River water at pH 5.

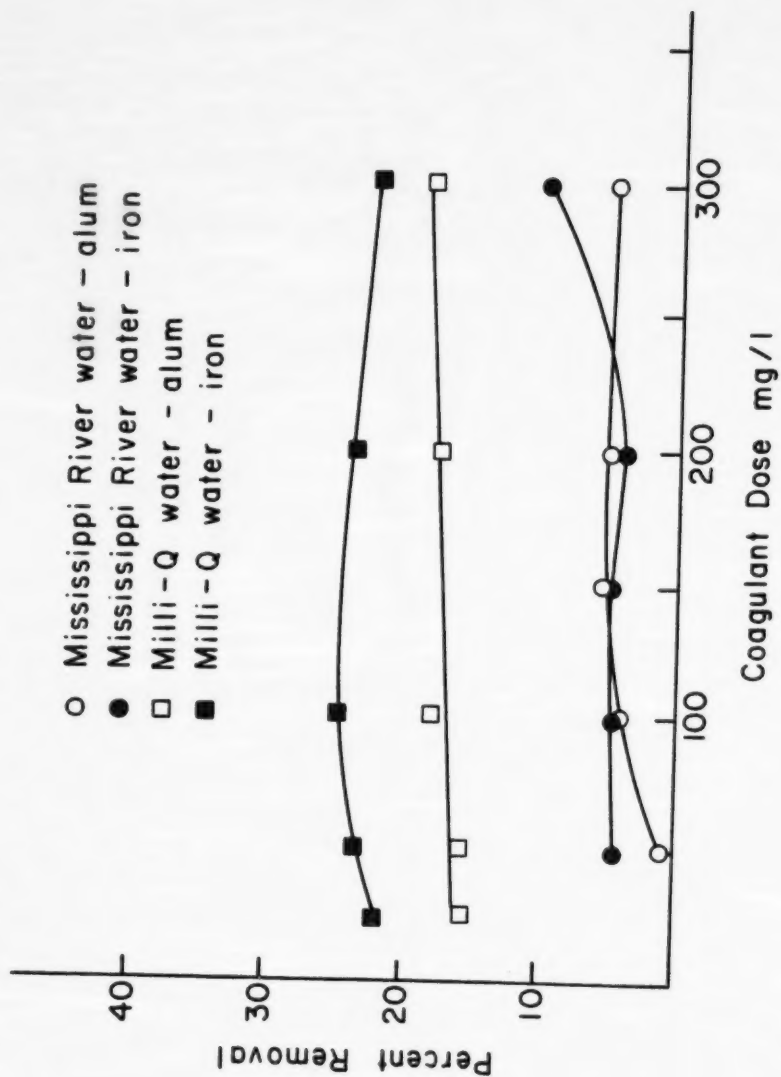


Figure 9. Dose effect for the removal of octanoic acid from Mississippi River water and milli-Q water at pH 5.

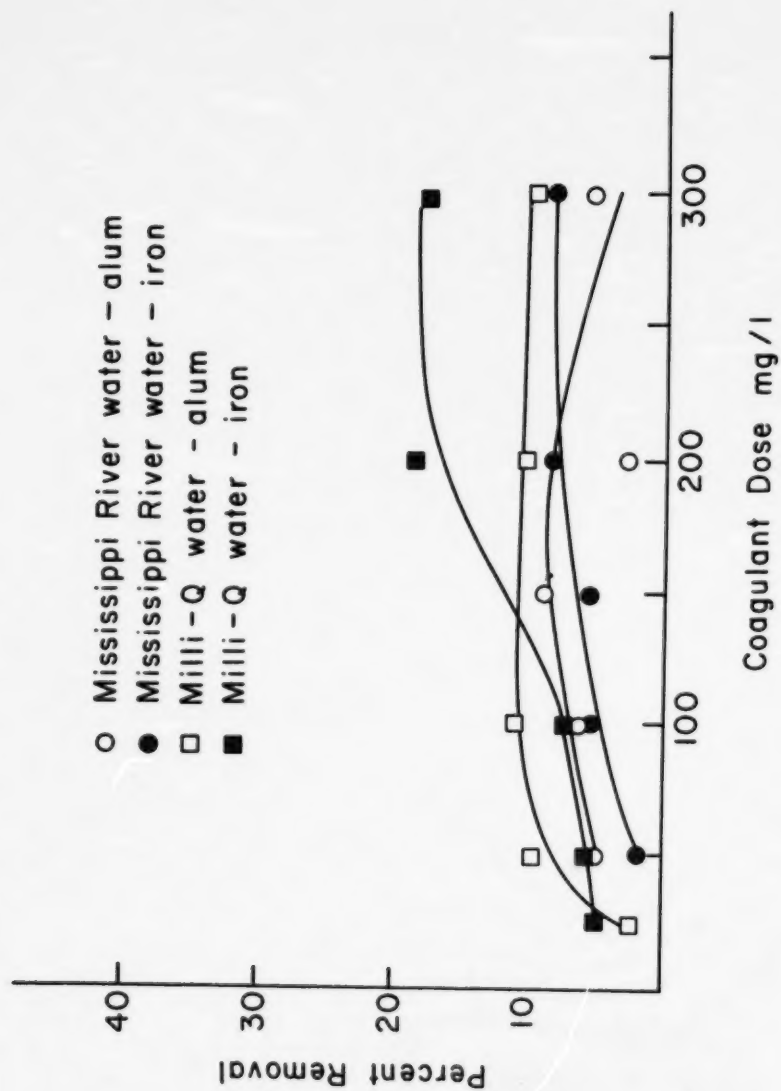


Figure 10. Dose effect for the removal of phenol from Mississippi River water and milli-Q water at pH 5.

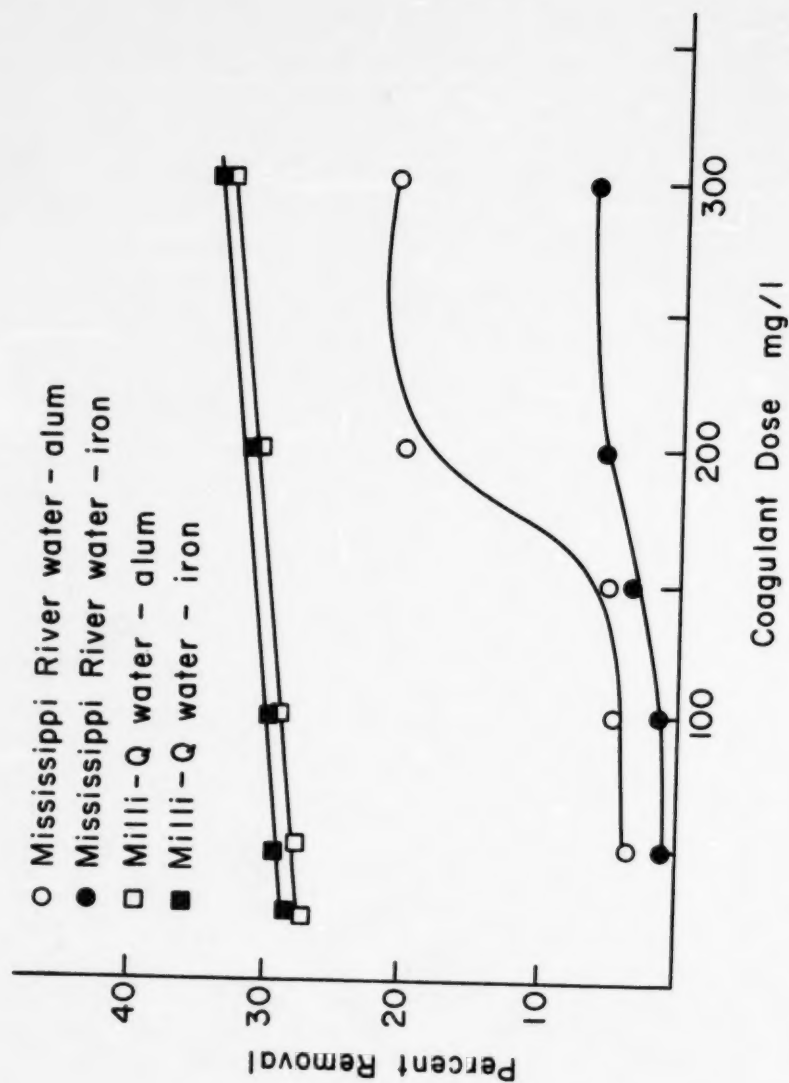


Figure 11. Dose effect for the removal of salicylic acid from Mississippi River water and milli-Q water at pH 5.

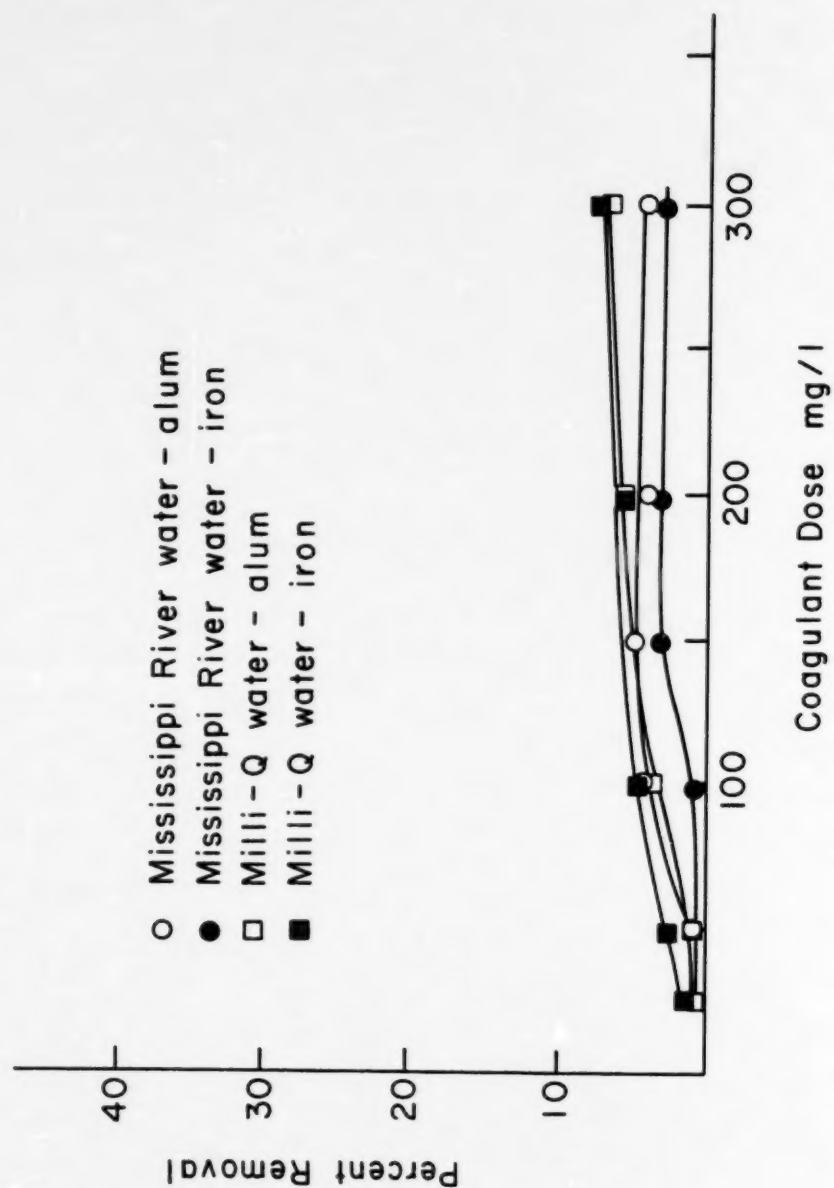


Figure 12. Dose effect for the removal of benzoic acid from Mississippi River water and milli-Q water at pH 5.

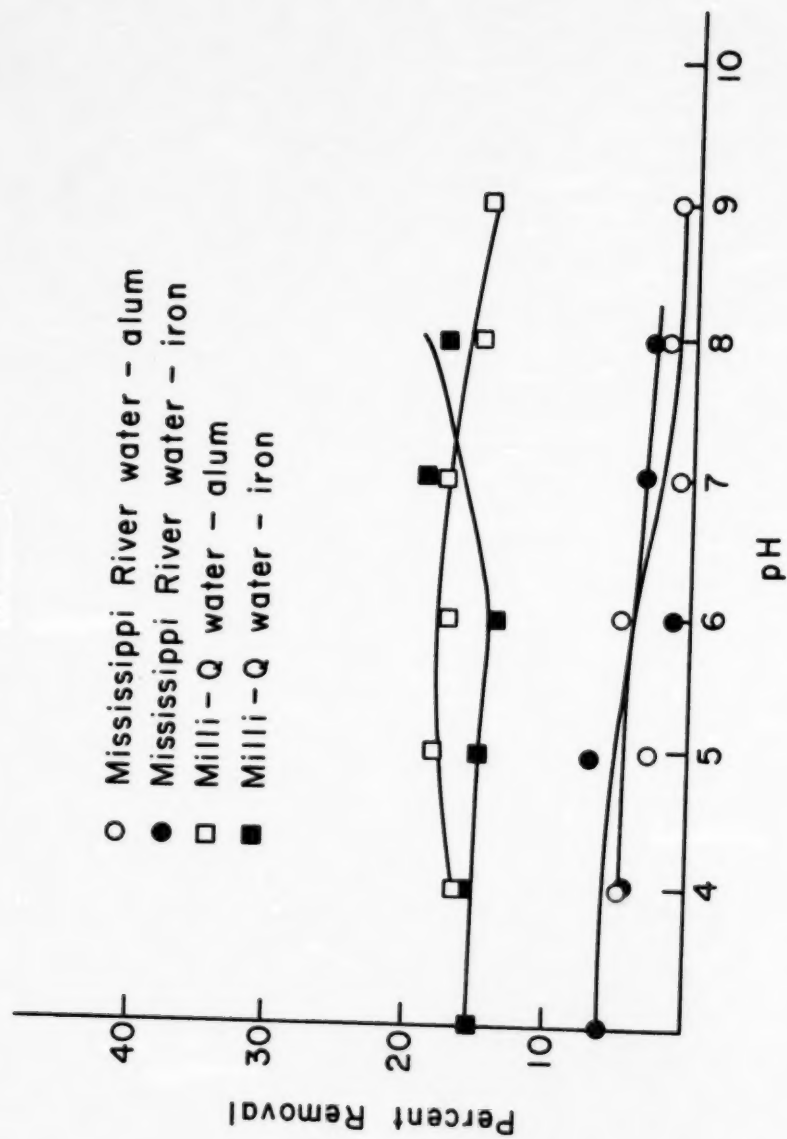


Figure 13. pH effect for the removal of octanoic acid from Mississippi River water and Milli-Q water with 200 mg/l of coagulant.

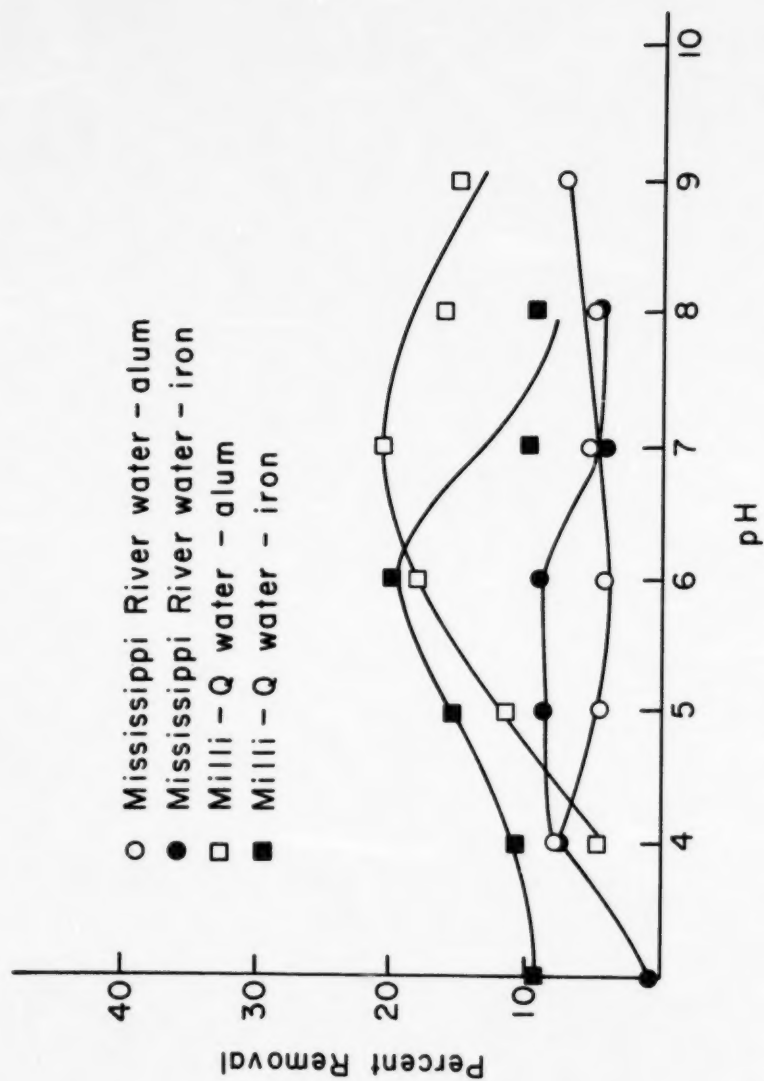


Figure 14. pH effect for the removal of phenol from Mississippi River water and milli-Q water with 200 mg/l of coagulant.

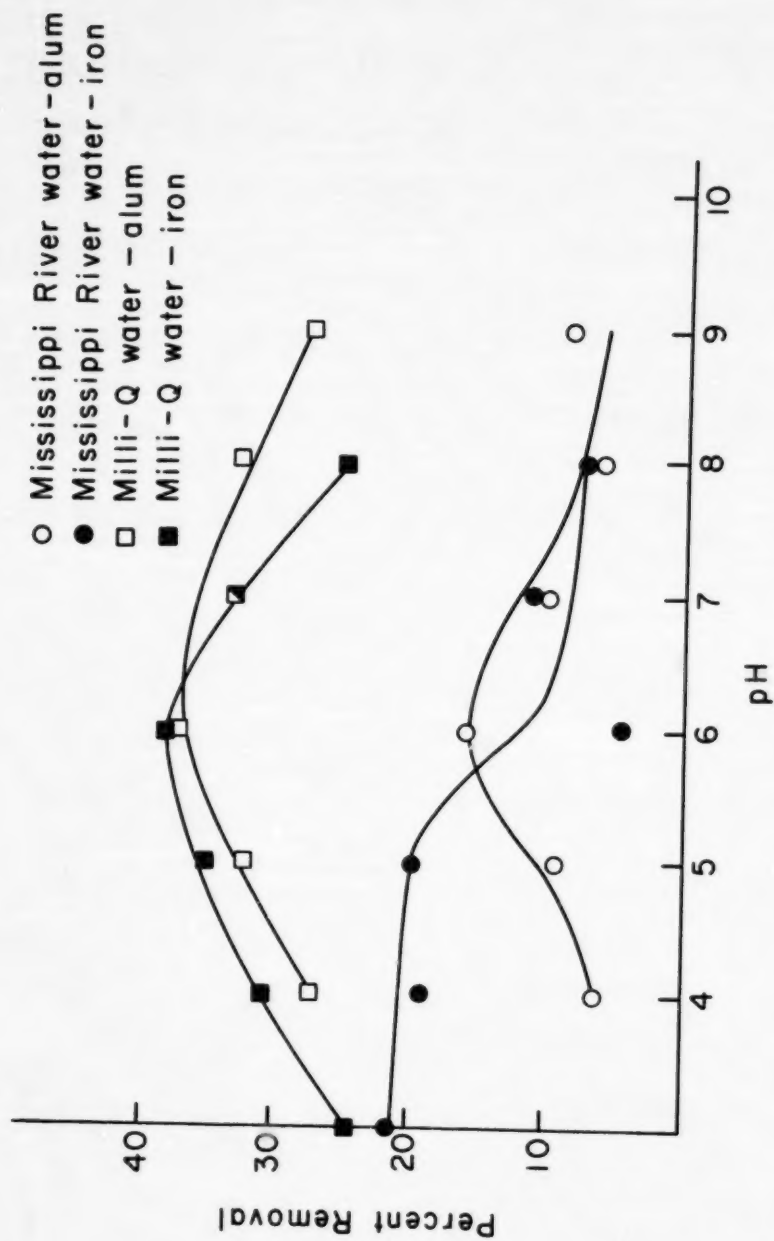


Figure 15. pH effect for the removal of salicylic acid from Mississippi River water and milli-Q water with 200 mg/l of coagulant.

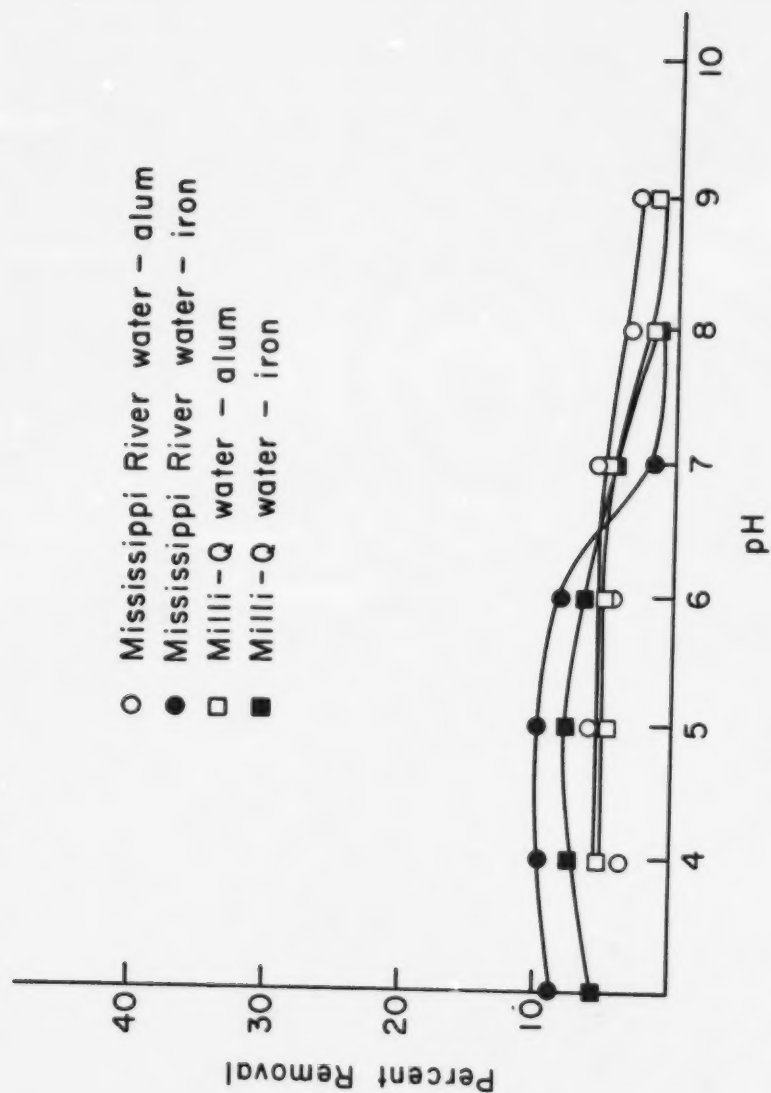


Figure 16. pH effect for the removal of benzoic acid from Mississippi River water and Milli-Q water with 200 mg/l of coagulant.

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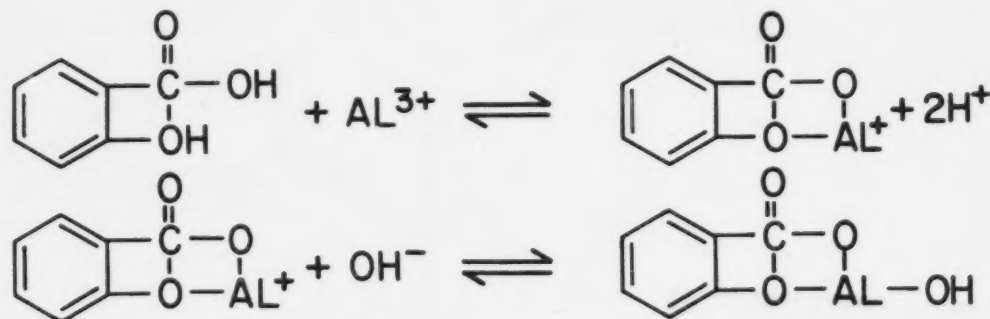
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whereas phenol and salicylic acid were best removed in the pH range of 5-7 and behaved more like the natural organic content of the river water. The observed pH dependence was more marked in the Milli-Q water than in the actual river water. Of the organic compounds examined, salicylic acid was removed best, phenol was marginally better removed than octanoic acid and benzoic acid was removed most poorly.

Comparison of the impact of the removal behavior of these model compounds provides some interesting insights on the mechanism of organics removal by coagulation. For example, the removal behavior of phenol and benzoic acid indicated that phenol was better removed. This suggested that the substitution of a phenolic-OH group was more significant in influencing removal by coagulation than a substituted carboxyl functional group. Further evidence that a substituted phenolic-OH group was beneficial was apparent in comparing the removal of benzoic acid with salicylic acid.

Octanoic acid was better removed than benzoic acid. This may result from the greater configurational entropy of the octanoic acid that allowed it to adopt a configuration that was more beneficial for removal by coagulation. The acidity of the carboxylic functional groups did not appear to significantly influence removal behavior of the organic compounds.

Stumm and Morgan (28) working with 5×10^{-3} molar concentration of salicylic acid and 3.4×10^{-3} molar concentration of aluminum proposed that salicylic acid was removed in a two-step complex formation reaction with aluminum ions. This reaction proceeds as follows:



Their work indicated that the positively charged salicylate complex was soluble and that precipitation did not occur until the second reaction had taken place to a significant extent. This occurred at a pH of approximately 5.5. As the pH was increased further, hydroxide ions displaced the salicylate ions in the aluminum complex.

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Other investigators have noted the similarities between metal complexation by fulvic and humic acids and the bidentate coordination by salicylic

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acid. These studies indicate the important role that phenolic hydroxyl groups may play in metal complexation by humic material in natural waters.

Hines and Barber (29) found that by blocking the non-carboxylic functional groups of fulvic acid, zinc complexation was reduced just as much as when the carboxylic groups were blocked.

Schnitzer and Skinner (29) conducted more complete studies on Cu^{++} , Al^{+++} and Fe^{+++} complexation by fulvic acid. They found that the greatest reduction in metal ion complexation by fulvic acid was achieved when phenolic OH groups and carboxyl groups were both blocked. The second greatest reduction was noted when either carboxyl or phenolic OH groups were blocked. The involvement of the phenolic OH group in metal complexation has also been demonstrated in potentiometric studies of humic and fulvic acids (29). The complexation of metals by the phenolic OH group releases otherwise untitratable H^+ ions into solution. It seems likely therefore that the coagulation of natural organics by alum and iron occurs following the formation of complexes involving both phenolic OH and ortho substituted carboxylic functional groups.

It was apparent that the presence of natural organics tended to reduce the effectiveness of removal of the trace organic compounds. This was noticeable for phenol, salicylic acid and octanoic acid, but little impact on benzoic acid removal was apparent. This may result from competitive effects. The natural organic content of Mississippi River water is rich in carboxyl and phenolic OH groups. In addition, the Mississippi River water may contain small concentrations of the model compounds tested and this would change the starting concentration and influence the observed removal behavior.

The addition of cationic polymer Purifloc C31 during coagulation with alum and iron did not significantly alter the removal behavior of the model compounds. Generally, as polymer was added in progressively higher concentrations, slight (1-2%) improvements in the removal of the model compounds were noted. However, the cost of polymer addition outweighed the benefit in improved removals of the model compounds.

Fractionation Studies

Four five liter volumes of reconstituted Mississippi River water were coagulated at different doses of alum and ferric sulfate, and one five liter volume of uncoagulated river water were fractionated into four molecular weight ranges by ultrafiltration. Millipore PT Series 90 mm membranes (Millipore Corporation, Redford, MA) with nominal molecular weight limits (nmwl) of 1,000, 10,000 and 100,000 were used. The fractionation technique utilized was the one described by Eisenreich, et al. (30).

Prior to the initiation of the fractionation study, the membranes were preconditioned by allowing them to soak in Milli-Q water for 24 hours. The ultrafiltration cells utilized were able to accommodate 500 mL portions of the water at one time. To further ensure the membranes were leaching as

little organic material as possible, the first 500 mL portion fractionated by each membrane was wasted. Also, to prevent any shift in the nominal molecular size cutoffs, only 250 mL of each 500 mL portion were passed through the membranes. The 1,000 nmwl membrane was operated at a pressure of 40 psig and the 10,000 and 100,000 nmwl membranes were operated with a pressure of 20 psig.

The actual fractionation scheme is delineated below. An initial sample volume of 5 liters was prepared. Five hundred mL were placed in the ultra-filtration cell containing the 100,000 nmwl membrane and pressure was applied. After 250 mL had passed through the membrane, the pressure was released and the retentate and the permeate were wasted. This procedure was repeated and the permeate and retentate were saved until the entire 5 liters had been utilized. The permeate was then applied to the 10,000 nmwl membrane in the same fashion, and the permeate from this membrane was in turn applied to the 1,000 nmwl membrane as depicted in Figure 1. One hundred mL samples of the permeate from each membrane and the initial river water were placed in glass bottles capped with aluminum foil and stored at 4°C until analyzed. Table 3 presents the results of the molecular weight fractionation. The fractions were calculated following the procedure outlined in Table 2. The results are presented pictorially in Figures 17 and 18.

TABLE 3. TOC VALUES OF MOLECULAR WEIGHT FRACTIONS

Water	TOC (mg/L)				
	>100K	10K-100K	1-10K	<1K	Total
200 mg/L Alum	0.0	0.1	3.8	2.2	6.1
200 mg/L $\text{Fe}_2(\text{SO}_4)_3$	0.2	0.8	2.2	2.7	5.9
50 mg/L Alum	0.0	0.0	5.2	3.3	8.5
50 mg/L Fe_2	0.0	0.0	5.0	3.1	8.1
Raw Water	0.2	1.6	11.2	3.5	16.5

Most of the organic content (TOC) of Mississippi River water was found in the 1 to 10K molecular weight range with the 1K molecular weight range comprising the next highest fraction. Relatively small amounts of TOC were observed in the molecular weight ranges greater than 10,000. This result corresponds favorably to results obtained by other investigators (30,31).

From the data presented in Table 3, percent removal of TOC was calculated for each molecular weight fraction. The results of these calculations are shown in Table 4. Table 4 illustrates that the higher molecular weight fractions are removed by both high and low doses of either alum or ferric

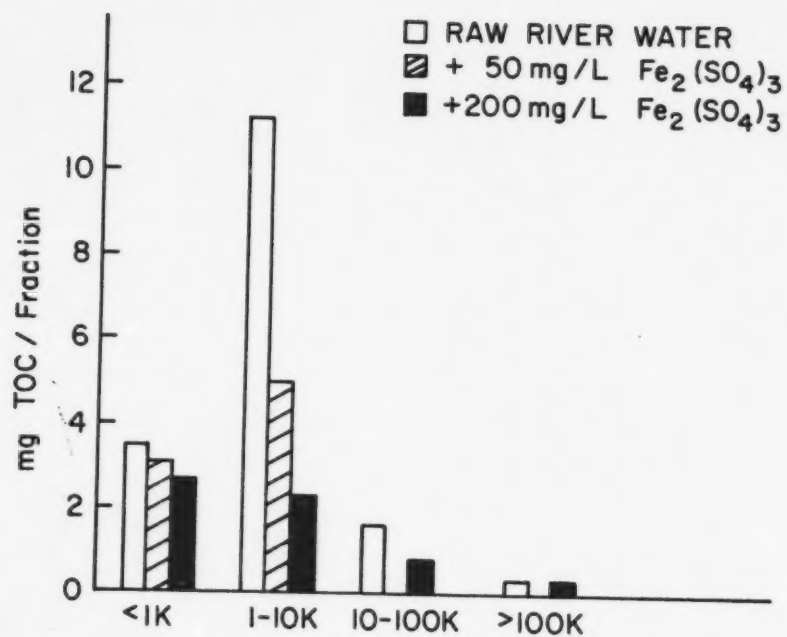


Figure 17. The influence of coagulation with iron on the removal of organics fractionated by molecular weight.

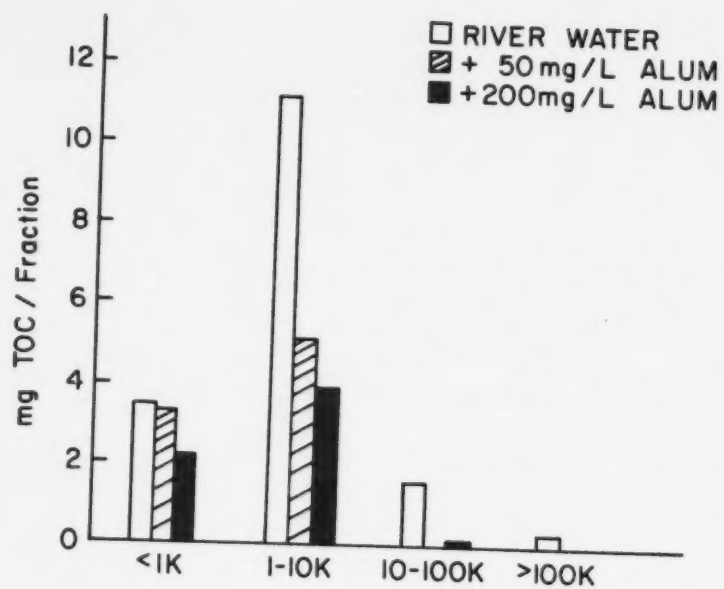


Figure 18. The influence of coagulation with alum on the removal of organics fractionated by molecular weight.

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sulfate. Removal of TOC in the 1-10K and <1K molecular weight ranges appeared to be dose related and significant percentage removals in these fractions were observed at the higher coagulant doses.

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TABLE 4. PERCENT REMOVALS OF TOC FOR VARIOUS MOLECULAR WEIGHT RANGES

Water

	>100K	10-100K	1-10K	<1K
200 mg/L Alum	100	94	66	37
200 mg/L $\text{Fe}_2(\text{SO}_4)_3$	0	50	80	23
50 mg/L Alum	100	100	54	6
50 mg/L $\text{Fe}_2(\text{SO}_4)_3$	100	100	55	11

The fractionation data also show relatively low removals for the low molecular weight fraction less than 1K. This indicates that the coagulation process is not as efficient in the removal of the very low molecular weight components. This observation agrees well with the observed removals of the model organic compounds which also showed between 5 and 20% removal generally.

The molecular weight distributions shown in Figures 17 and 18 indicate that some organics were found in the higher molecular weight range when higher coagulant doses were used. This was especially true for iron. It is possible that at higher iron concentrations iron-organic interactions alter the molecular weight distribution by promoting the formation of higher molecular weight complexes that are still too small to be removed by filtration.

In summary, the coagulation process removed higher molecular weight compounds most effectively and reduced the concentration of lower molecular weight functions. This suggests that the coagulation process may be employed effectively as a pretreatment before water is applied to activated carbon. Other investigators have noted that higher molecular weight humic substances are not removed very effectively by activated carbon while lower molecular weight compounds are readily removed (32). The coagulation and adsorption processes should therefore complement one another and the best removal of organics may be achieved by a combination of the two processes.

A more complete characterization of Mississippi River water and the impact of coagulation is reported in Section 7.

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SECTION 5

COAGULATION STUDIES WITH POLYMERS AND OTHER ADDITIVES

INTRODUCTION

Studies were conducted to evaluate whether coagulation with alum or ferric sulphate could be improved by coagulant aids or process changes when the process was operated for organics removal. Studies were conducted on a Mississippi River water sample which had been freeze concentrated. Water samples were reconstituted with organic-free distilled water to provide a test water of invariant quality. Details of the freeze concentration technique are reported in Section 3 of this report.

Semmens and Field (36) characterized the removal behavior of alum and ferric sulphate when these coagulants were used to treat Mississippi River water. This study extends the work of these investigators.

COAGULANT AIDS

Jar test studies were conducted with a variety of EPA approved polymers having different chemical and physical characteristics. The selected polymers varied in charge, molecular size, and chemical structure as shown in Figure 19. These polymers were evaluated as coagulant aids in studies where alum and ferric sulphate were the primary coagulants. Performance was evaluated by organics removal (UVA, TOC, and THM removals). In addition, some studies were conducted to evaluate the effectiveness of polymers as primary coagulants.

A single batch of Mississippi River water (MRW) was collected on April 30, 1980 and freeze-concentrated. The reconstituted water was employed for all the studies reported in this section of the report unless otherwise noted. Prior to any polymer addition studies, the dose-response relationship for organic removal was evaluated for the water sample for alum and ferric sulphate. The results are presented in Figure 20. Organics removal was evaluated by TOC, UVA and THMFP reduction following coagulation and filtration. The reduction of these parameters by coagulation showed excellent correlation as previous studies had also indicated. As such, only ultraviolet absorbance was employed to screen polymer performance in many studies. Analysis of the alum and ferric sulphate data in Figure 20 revealed that organics removal by alum increased with increasing dose to about 50 mg/L and then plateaued, whereas ferric sulphate was not effective as a coagulant until the dose exceeded 20 mg/L. Organics removal also plateaued for ferric sulphate above a dose of 60 mg/L.

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POLYMER	CHARGE	APPROX. MOL. WT.	STRUCTURE
Arco 6320P	highly cationic	20,000	Polyquaternary Amine $\left[\text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{N}^+}} - \text{Cl}^- \right]_x$
Arco 6340P	highly cationic	100,000	
Arco 6360P	highly cationic	300,000	
Betz 1190	highly cationic	low	
Arco 6450P	highly cationic	medium	PolyDADMAC $\left[\text{CH}_2 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 \right]_x$
Calgon Catfloc T	highly cationic	150,000	
Am. Cyanamid Man-nifloc5910	highly cationic	500,000	
Dow Purifloc C-31	highly cationic	--	Polyamine $\left[\text{CH}_2 - \underset{\text{C}=\text{O}}{\underset{\text{NH}_2}{\text{CH}}} \right]_x \left[\text{CH}_2 - \underset{\text{C}=\text{O}}{\underset{\text{NH}}{\underset{\text{CH}_2}{\text{N}}}}} - \text{CH}_2 \right]_y$
Arco 6815P	weakly anionic	very very high	Polyacrylamid-Acrylic Acid $\left[\text{CH}_2 - \underset{\text{C}=\text{O}}{\underset{\text{NH}_2}{\text{CH}}} \right]_x \left[\text{CH}_2 - \underset{\text{C}=\text{O}}{\underset{\text{OH}}{\text{CH}}} \right]_y$
Calgon Ca-243	Anionic	--	Structure unavailable from manufacturer
Calgon Ca-233	Nonionic	--	

Figure 19. Characteristics of Selected Polymers

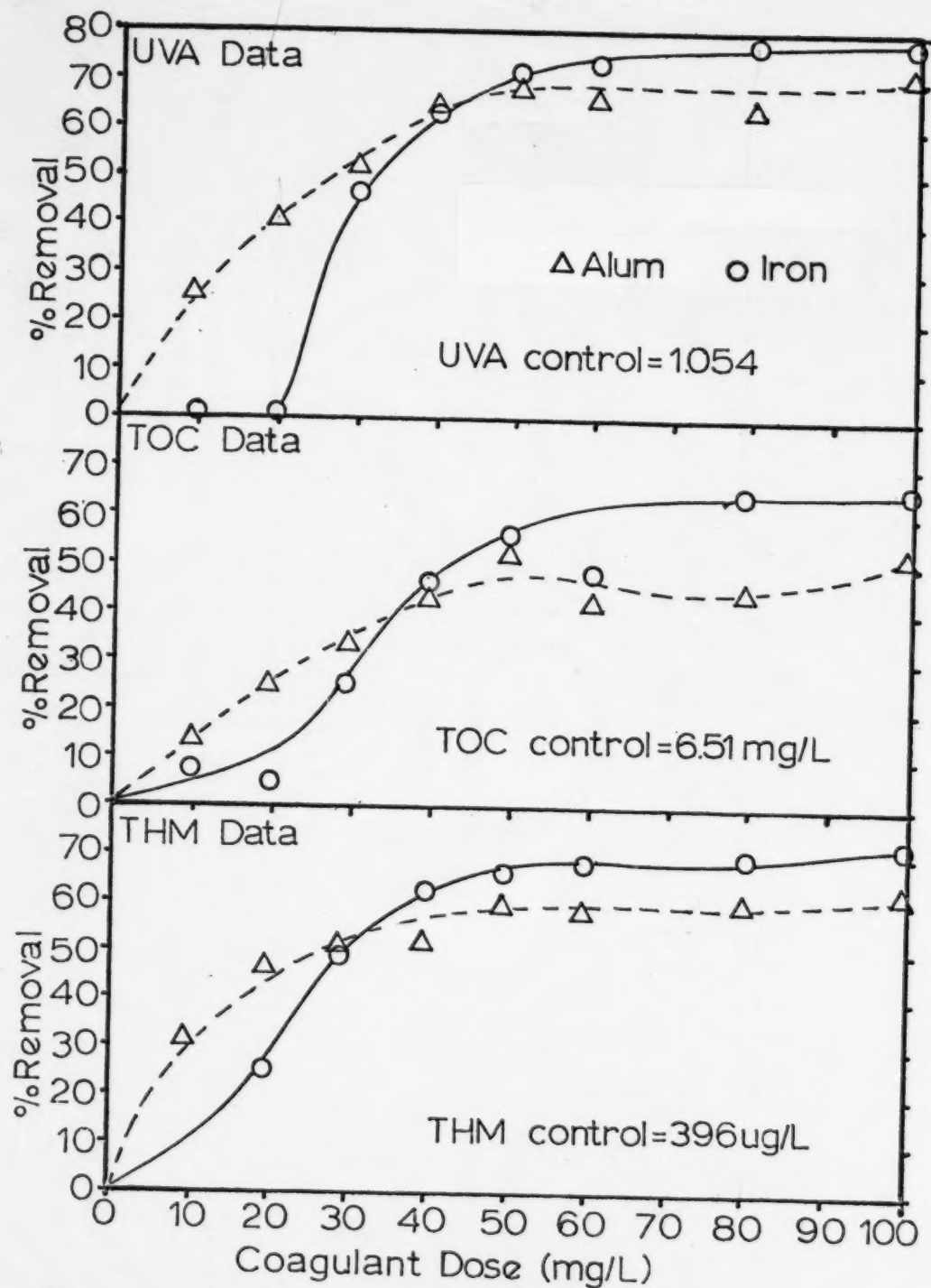


Figure 20. Impact of coagulant dose on organics removal from MRW

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Two coagulant doses were selected for study with coagulant aids. A dose of 80 mg/L was chosen to reflect a condition of maximum organics removal by both coagulants and 20 mg/L was chosen as being representative of the region of the curve where removal was dose dependent. In addition, at 20 mg/L, alum and iron exhibited a difference in behavior with alum giving about 25% TOC removal, whereas iron only gave approximately 5-10% removal.

Cationic Polymers

A dose range of 0 to 5 mg/L polymer was tested in conjunction with both 20 and 80 mg/L of primary coagulant. An example result is shown in Figure 21 for polymer addition to ferric sulphate and a very similar result was obtained with alum as the primary coagulant as shown in Figure 22.

These studies on polymer addition indicated that no benefit was gained from any polymer dose when the primary coagulant dose was 80 mg/L. Some improvement in performance was noted as a result of polymer addition at the lower coagulant dose (20 mg/L). This effect was most striking when the polymer was used in conjunction with iron as shown in Figure 21. TOC removal was increased by approximately 30% with a polymer addition of about 2 mg/L. Corresponding improvement in removals were also noted when THMFP and UVA were measured. When the polymer was used in conjunction with alum, the improvement was only marginal as shown in Figure 22, and at best only accounted for an additional 5% removal. Interestingly, the addition of polymer to the ferric sulphate had the effect of improving removals until they equalled the performance achieved by alum alone. With the addition of >2 mg/L polymer, there was essentially no difference in performance between 20 mg/L of either alum or ferric sulphate.

Previous studies indicate a good deal of variation in system response to cationic polymers, and Cohen *et al.* (96) stressed the varying effectiveness of polymers in the treatment of different waters. Black and Williams (41) and Ayers (98) found polymer improved coagulation with ferric salts more effectively than with alum. However, other researchers have found the alum/polymer combination superior (59,61,101).

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These results suggest that the polymer acts in a similar way to the addition of excess coagulant. The polymer may assist in partial adsorption and charge neutralization with bridging between colloidal organics. Thus, at low doses of coagulant, many organics are incompletely neutralized or complexed with iron or aluminum hydrolysis products and they do not aggregate effectively during the coagulation-flocculation process. The addition of polymer may neutralize some of the excess negative surface charge and improve flocculation by bridging. However, at higher coagulant doses, the organics are likely to be completely complexed by coagulant and the precipitation of insoluble $Al(OH)_3$ encourages aggregation and removal of the organics. Under these circumstances, the addition of polymer has no value for organics removal although it may still improve the settling characteristics, dewaterability and the volume of the sludge generated. These latter benefits were not evaluated in this small scale study.

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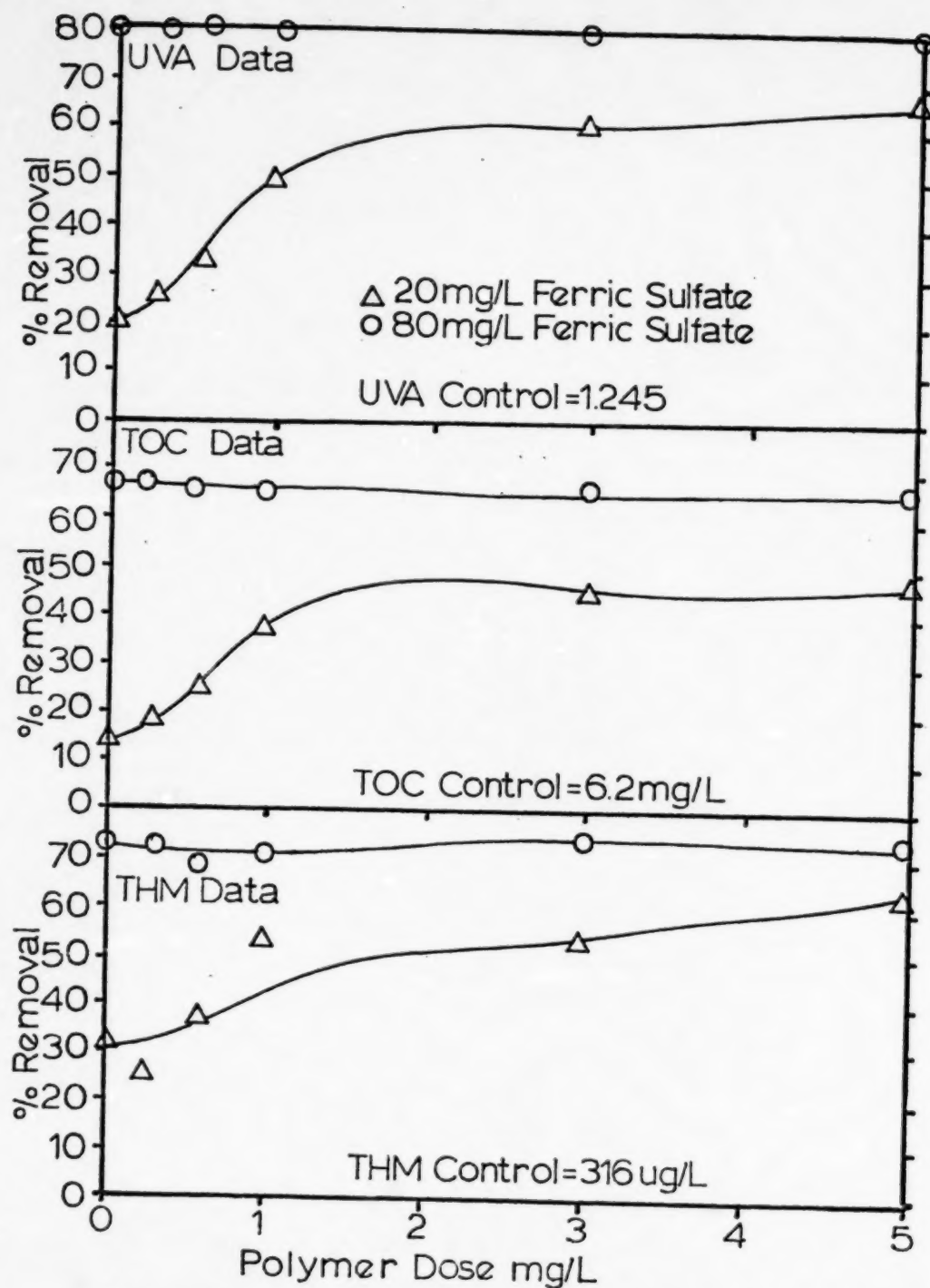


Figure 21. Effect of Arco 6360P dose plus iron on organics removal from Mississippi River Water pH = 5.0.

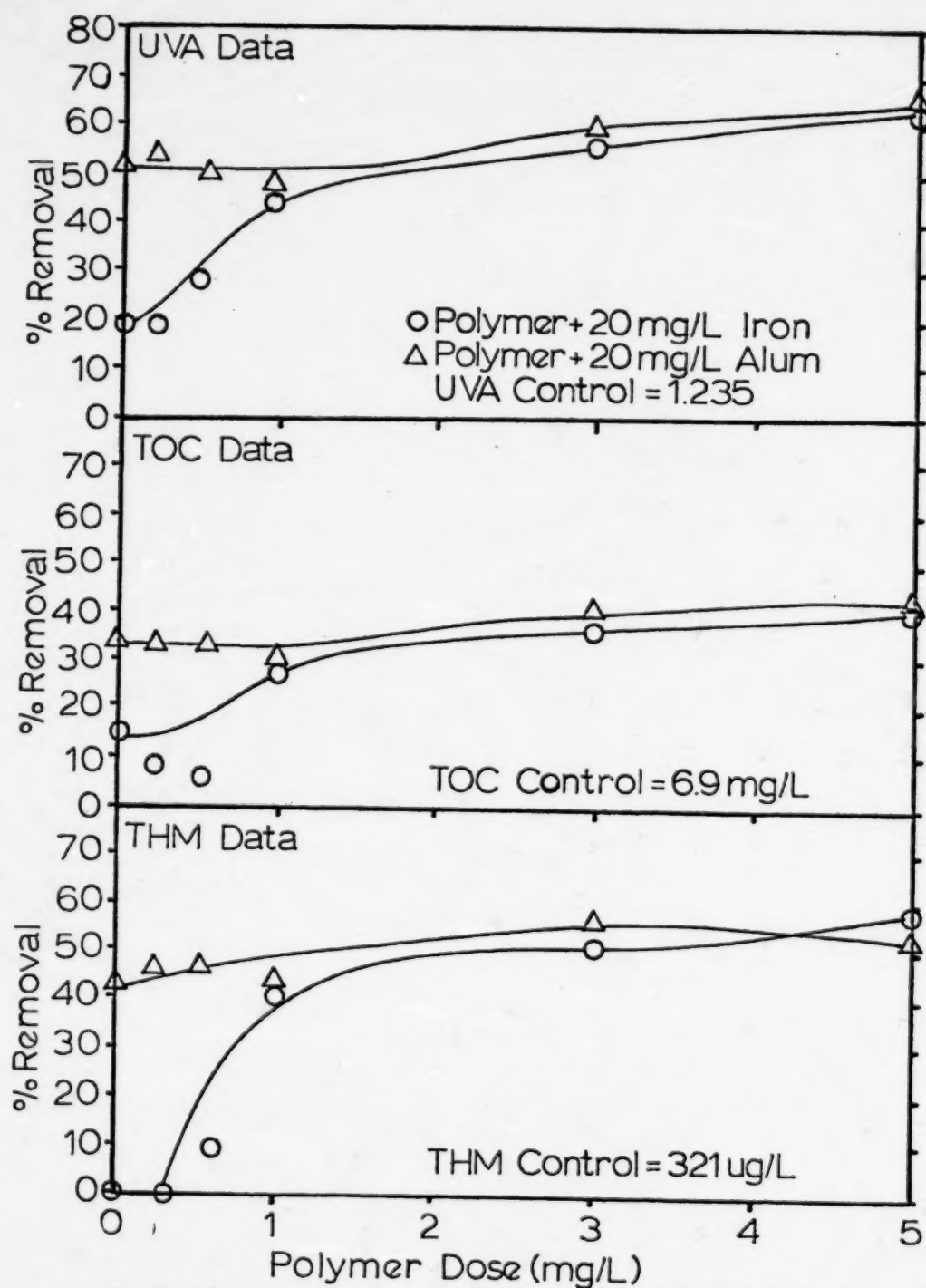


Figure 22. A comparison of organics removal from Mississippi River water by polymer plus alum and polymer plus iron, pH = 5.0. Polymer = Arco 6340P.

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A selection of cationic polymers were tested, and an attempt was made to study the effect of polymer structure on organics removal. However, the polymers tested were all commercially manufactured products and specific information concerning structure, degree of hydrolysis, and percent active material was generally considered propriety information. Dr. Mangravite (Arco Performance Chemicals Co.) was most helpful, however, in both providing polymers and recommending other manufacturers' polymers that would enable a comparison of a variety of polymer structures. It was with his help that the polymers presented in Figure 19 were selected for study.

The impact of polymeric structure upon organic removal effectiveness was evaluated by comparing the results of studies in which Arco 6340 P and Arco 6450 P were tested as coagulant aids. The former polymer is a polyquaternary amine in which the amine functional group is actually incorporated within the polymer chain, whereas the latter polymer (6450 P) is polydiallodimethylammonium chloride (Poly DADMAC) in which the quaternary amine group is attached to the polymer chain by methylene bridges.

These two cationic polymers were chosen since they have been examined in several earlier studies (59,62,103) and since they are widely employed in water treatment practice. The results of the study are presented in Figure 23. These results clearly indicate the superiority of the polyquaternary amine. However, when two other poly DADMAC's from different manufacturers were tested and compared with the polyquaternary amine, their performance was comparable with the latter polymer. Figure 24 compares the UVA removals for the polyquaternary amine Arco 6320 P, and two poly DADMAC polymer: Catfloc T (Calgon Corporation) and Magnifloc 591 C (American Cyanamid Company). The organics removal behavior exhibited by these two different polymer structures appears quite comparable.

The Arco polyquaternary amine resin has a very high charge density which is approximately 300% higher than the charge density on the Arco poly DADMAC. The former polymer was expected to perform more effectively than the latter polymer if a mechanism of adsorption and charge neutralization was involved. The relative charge density of the poly DADMAC polymers provided by other manufacturers was not known, although their performance suggests that they had a higher charge density than the Arco poly DADMAC. No measurements were made to verify this, however, and the differences in polymer characteristics from different supplies may preclude such a simple explanation.

The effect on organics removal of increasing polymer molecular weight within a given polymer structure was studied and is reported in Figures 25 and 26. Three polymers of the polyquaternary amine structure (Arco 63 series) having molecular weights of approximately 20,000 (Arco 6360 P), 100,000 (Arco 6340 P) and 300,000 (Arco 6360 P) were tested. It appeared that some benefit derived from a higher polymer molecular weight at low doses of iron. No UVA removal was noticed with 20 mg/L and 1 mg/L of Arco 6320 P (>20,000 MW) but 40-50% removal was observed with the higher molecular weight polymers of the same general type. Since polymer bridging is improved when larger polymer molecules are used, it suggests that at low ferric sulphate doses the addition of higher molecular weight polymers may be more effective since

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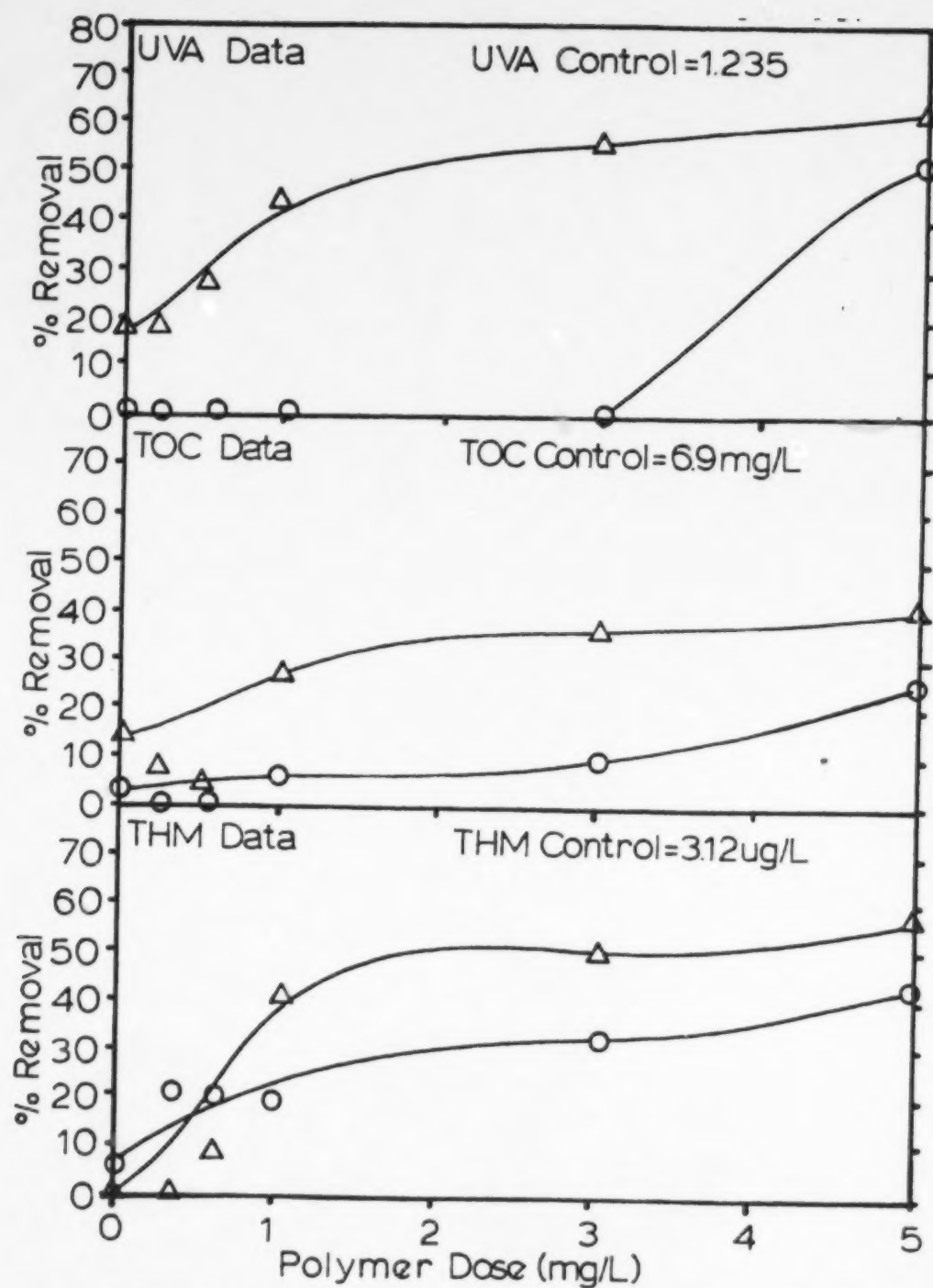


Figure 23. A comparison of organics removal from Mississippi River water by a polyquaternary amine and a poly-DADMAC polymer in conjunction with 20 mg/L iron. pH = 5.0, Δ = 6340, O = 6450P

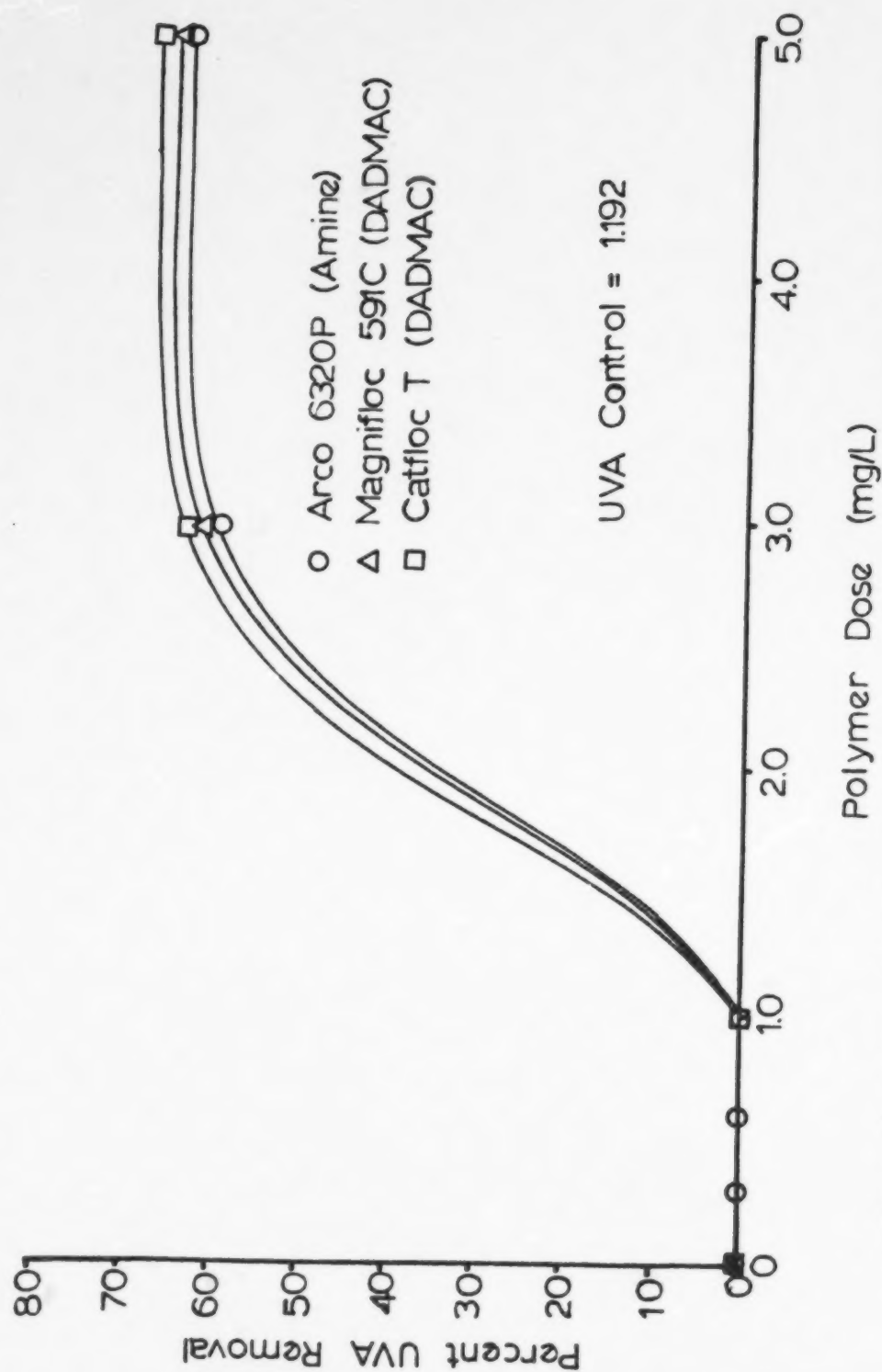


Figure 24. A comparison of UVA removal by a polyquaternary amine and 2 polyDADMAC polymers in conjunction with 20 mg/L iron.

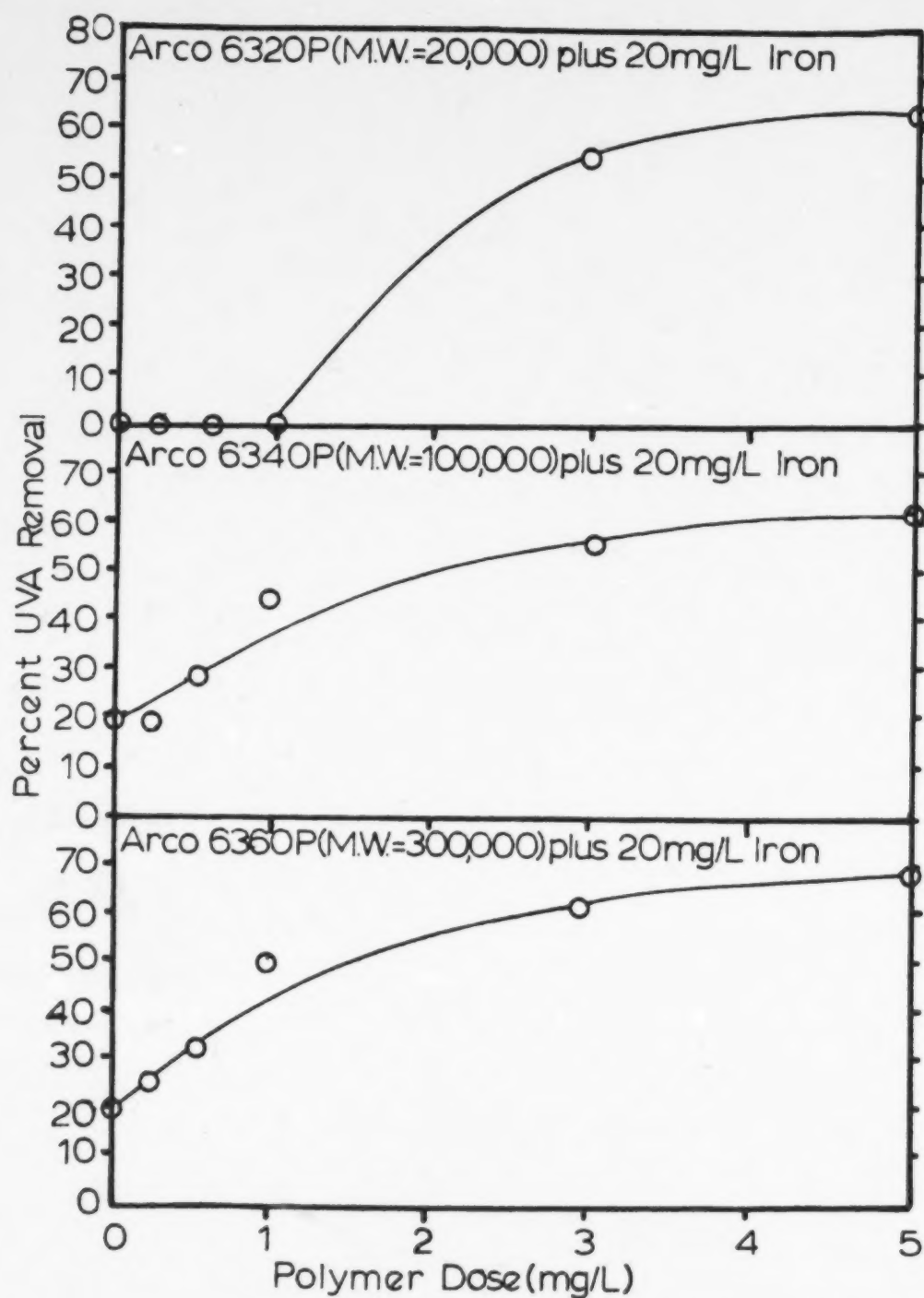


Figure 25. The effect of increasing polymer molecular weight within the polyquaternary amine structure on UVA removal. Control UVA = 1.040

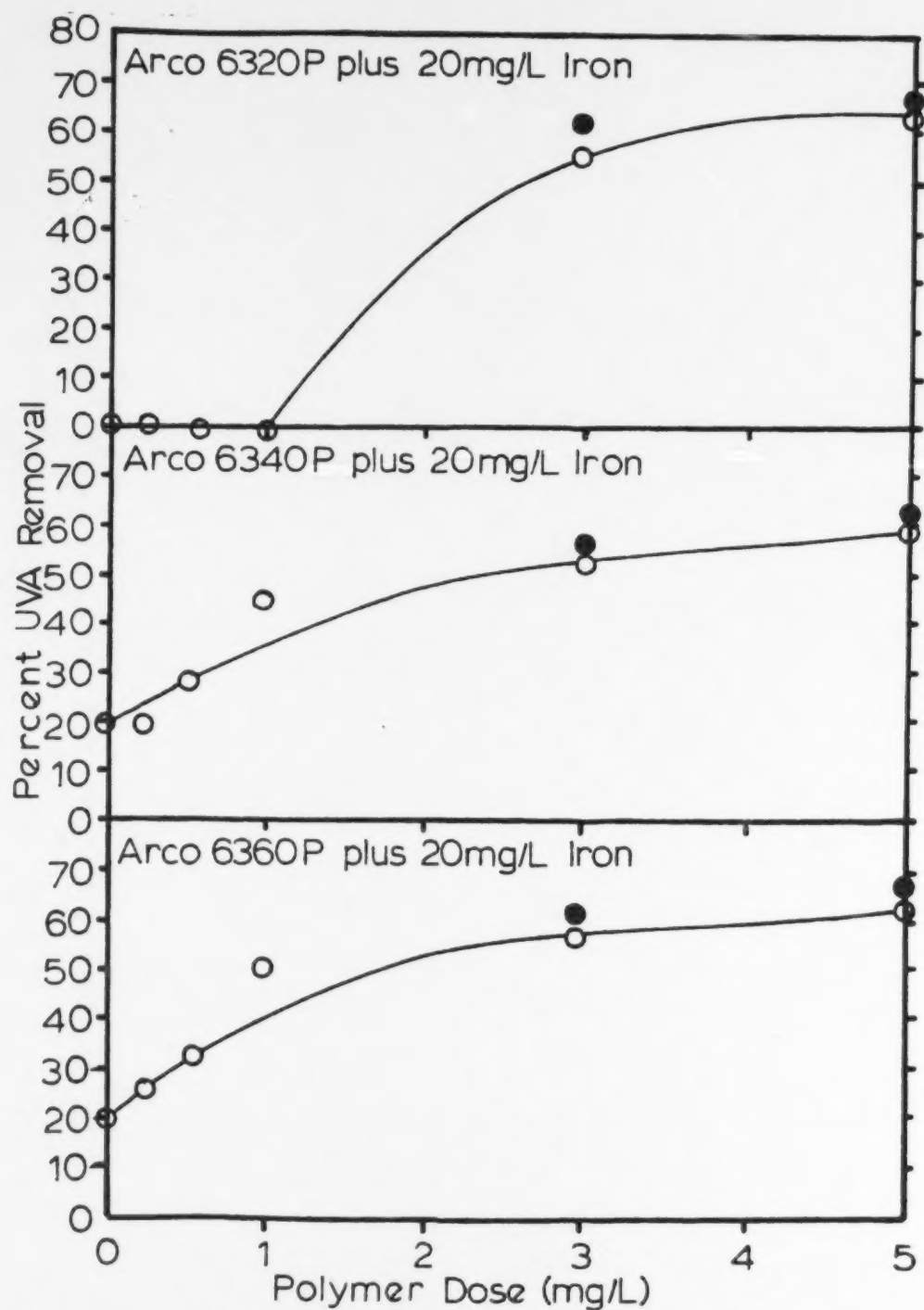


Figure 26. The effect of continuous addition of polymer as opposed to a one-shot addition on UVA removal

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they adsorb to the organics and are better able to cause aggregation and removal of the partially coagulated organics at low polymer doses. At higher polymer doses there was no significant difference in the observed behavior for the different molecular weights.

Tests were also conducted to determine if the way in which a cationic polymer was added to the water impacted organics removal. Arco 63 series polymers were tested in single dose additions prior to ferric sulfate, with the ferric sulfate, and immediately after, 10 seconds after and 2 minutes after the ferric sulfate addition. No apparent benefit was observed by changing the order of addition. Regardless of when the polymer was added, 20 mg/L ferric sulfate plus 3 mg/L Arco 6320 P gave UVA removals on the order of 55 percent.

Edzwald et al. (59) also found that the order of chemical addition was not critical for the coagulation of a humic acid suspension with alum and a cationic polymer.

In another test the polymer dose was split in five equal doses and injected at equal time intervals into the jar during the slow mix. This continuous addition of polymer produced a much larger and more settleable floc, and in most cases slightly increased organics removals. In Figure 26 the shaded symbols indicate continuous addition of Arco 63 series polymers to water in conjunction with 20 mg/L ferric sulfate. Only the 3 and 5 mg/L dosages were added in this manner. The slight increase in organics removal evidenced in Figure 26 was consistent with the observed trend in the TOC and THM data as well. Theoretically, the addition of several small amounts of flocculant as opposed to one large dose should provide for a more adequate dispersion of polymer and optimize polymer adsorption, thus leading to a more efficient incorporation of the primary particles into flocs (97).

Anionic, Non-ionic Polymers

Several coagulant aids, including anionic and non-ionic polymers, clay and activated silica were tested in conjunction with alum and ferric sulfate. The anionic polymer of polyacrylamid and acrylic acid (Arco 6815) was selected for study as it is frequently used in water treatment practice (104,105). This polymer showed no beneficial effect in removing organics with either ferric sulfate or alum at any dose. The same anionic polymer was tested in conjunction with ferric sulfate and a cationic polymer (Arco 6320 P). Again the anionic polymer, while possibly producing a larger more settleable floc, had no consistent impact on organics removal. These results are reported in Figure 27. In these tests the anionic polymer was added during the rapid mix immediately following the ferric sulfate (and cationic polymer) additions.

In another test, an anionic polymer (Calgon CA-243) was added 30 seconds after ferric sulfate addition. The results, presented in Figure 28, show that increasing the dose was actually detrimental to UVA removal both at 20 and 40 mg/L of ferric sulfate. A non-ionic polymer by the same manufacturer (Calgon CA-233) was also tested in conjunction with 20 and 40 mg/L of ferric sulfate. The results also showed that increasing the polymer dose resulted

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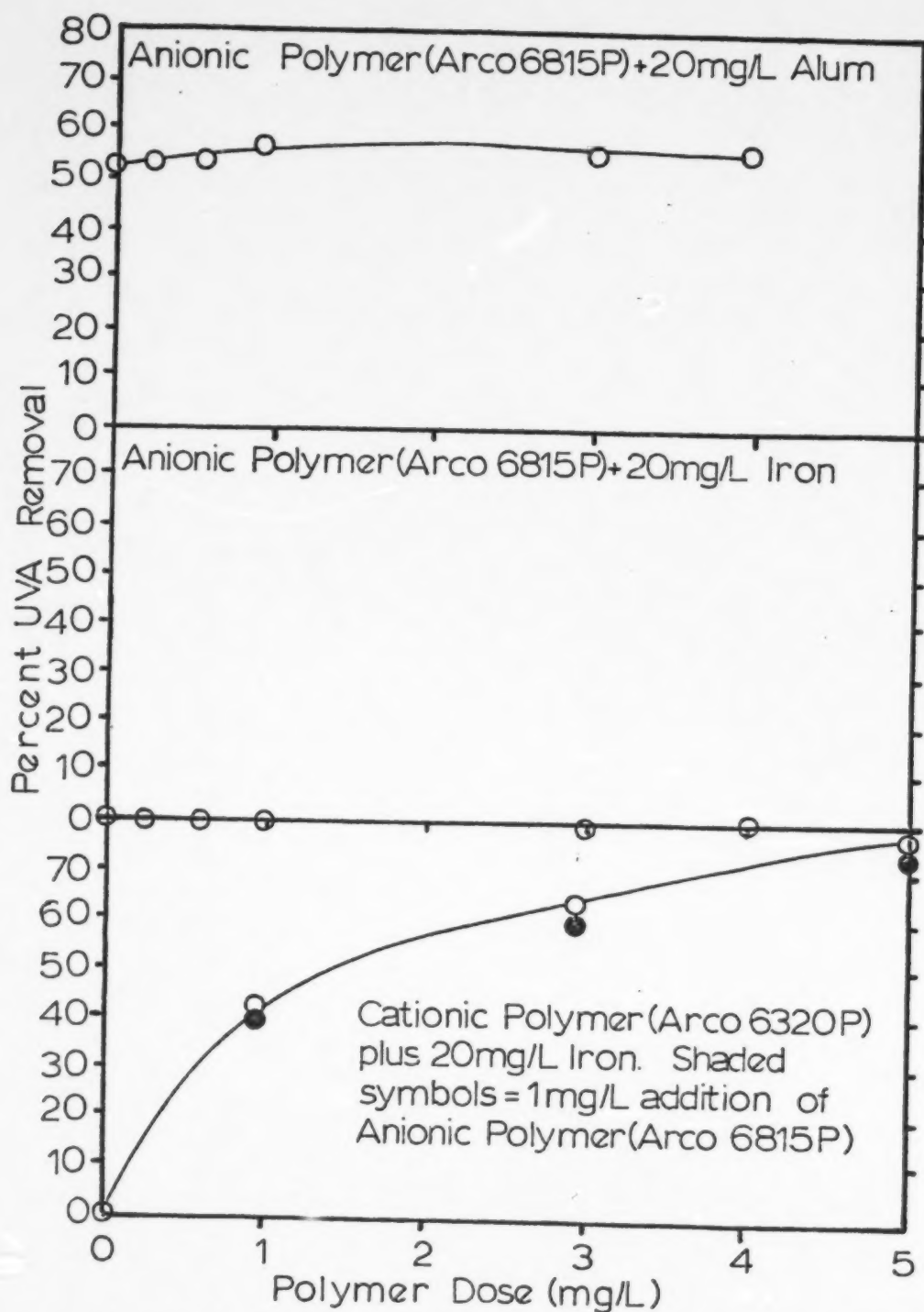


Figure 27. The effect of an anionic polymer in conjunction with alum, iron and iron/cationic polymer on UVA removal. (UVA control = 1.265)

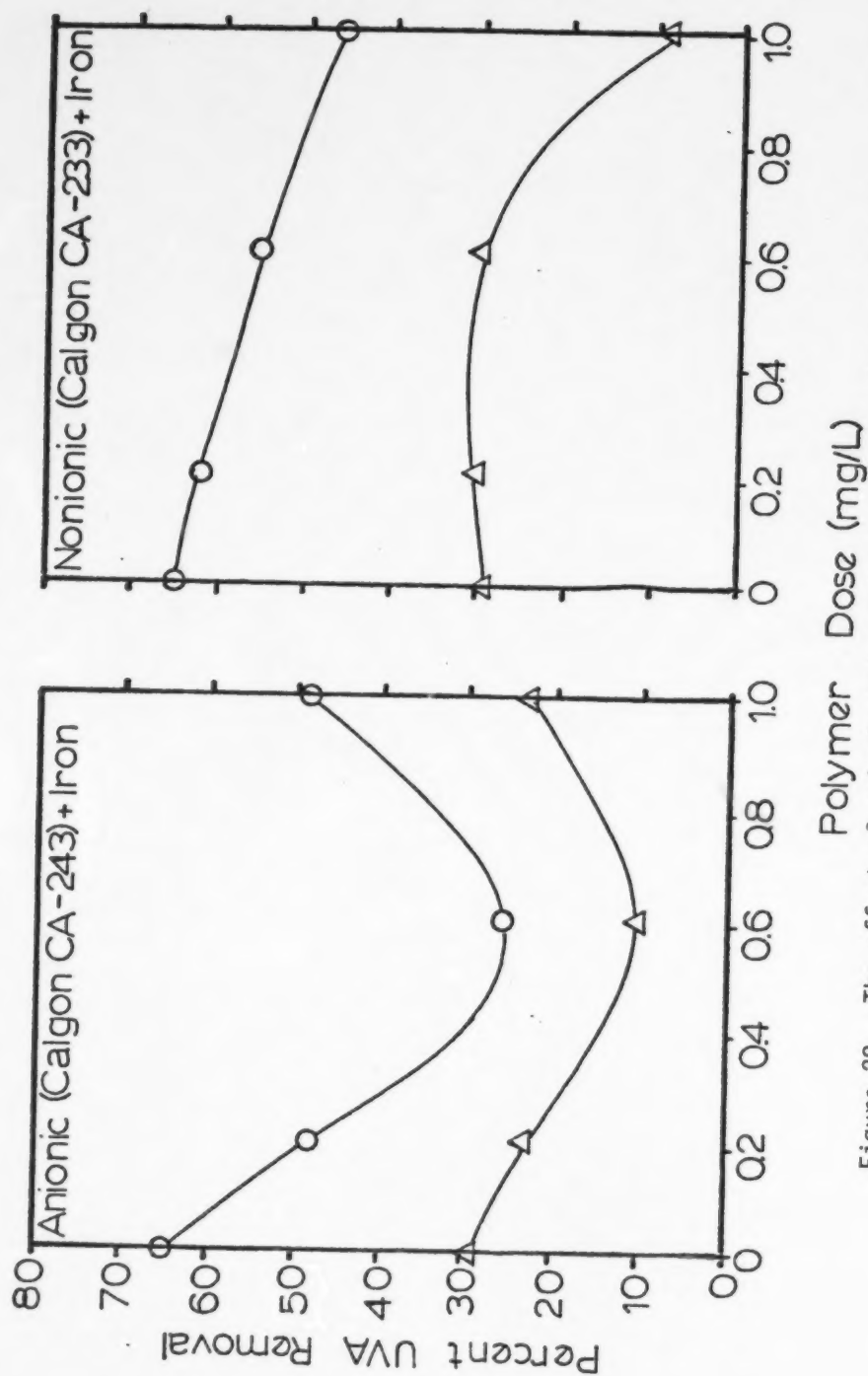


Figure 28. The effect of anionic and non-ionic polymers in conjunction with iron on UVA removal. UVA control = 0.793, Δ = 20 mg/L iron, $\circ$ = 40 mg/L iron.

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in a decline of UVA removal as shown in Figure 28. Both of these polymers were only tested to their maximum allowable dose of 1.0 mg/L.

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These results somewhat contrast those of other investigators who found that anionic and non-ionic polymers may be quite beneficial to the coagulation process (59,60,61,62). These discrepancies may be attributable to the fact that these investigators again used prepared suspensions of either humic acid or silica, and in some cases gaged flocculation efficiency by the removal of turbidity. Good turbidity removal does not always correspond with good organics removal (5).

The inability of anionic and non-ionic polymers to improve organics removal by low coagulant doses probably stems from their inability to interact successfully with the organic content of the water. Anionic polymers have been found effective in removing negatively charged colloids since polymer-colloid adsorptive forces may overcome the electrostatic repulsive forces (15). However, Haff (61) and Edzwald et al. (59) found that anionic polymers showed little or no chemical interaction or removal of humic acid when used in conjunction with alum.

Clay Addition

The use of clays to assist coagulation has historically been associated with low turbidity, low hardness waters. More recently it has been used successfully on Missouri River water and on certain colored waters (58). In addition to adding more nuclei for collision and subsequent aggregation, clays have been known to chemisorb some organics compounds (11,24).

In this experiment, a cold water bentonite clay (Nalco 8152) was used in conjunction with a polyquaternary amine cationic polymer (Nalco 8101). The polymer was evaluated as a primary coagulant and as a coagulant aid with ferric sulfate as the coagulant. In both experiments the clay was introduced into the rapid mix just before the addition of the other chemicals.

When used with the cationic polymer, the clay was dosed at 10 mg/L and the polymer dose ranged between 0 and 20 mg/L. As evidenced in Figure 29, the clay had a pronounced effect on organics removal above a polymer dose of 5 mg/L. At this dose, organic removal efficiencies for polymer alone began to decline, probably as a result of overdosing and restabilization. The clay appeared to prevent restabilization and allowed UVA removals to increase to a maximum of 40% at polymer doses between 15 and 20 mg/L.

When used with both ferric sulfate and polymer, the clay was again dosed at 10 mg/L. The ferric sulfate dose was preset at 20 mg/L and the polymer dose was varied from 0 to 5 mg/L. The results of this study are presented in Figure 30. The effect of the clay was to improve organics removal at lower polymer doses. At a polymer dose of 5 mg/L, the addition of clay had no beneficial impact on organics removal beyond that achieved with polymer and ferric sulfate alone. Comparison of Figure 30 with the removal behavior of Arco 6320P and ferric sulfate in Figure 25 indicated that Nalco 8101 polymer gave poorer organics removal performance even with clay addition. In this light, the Nalco polymer was excluded from further testing.

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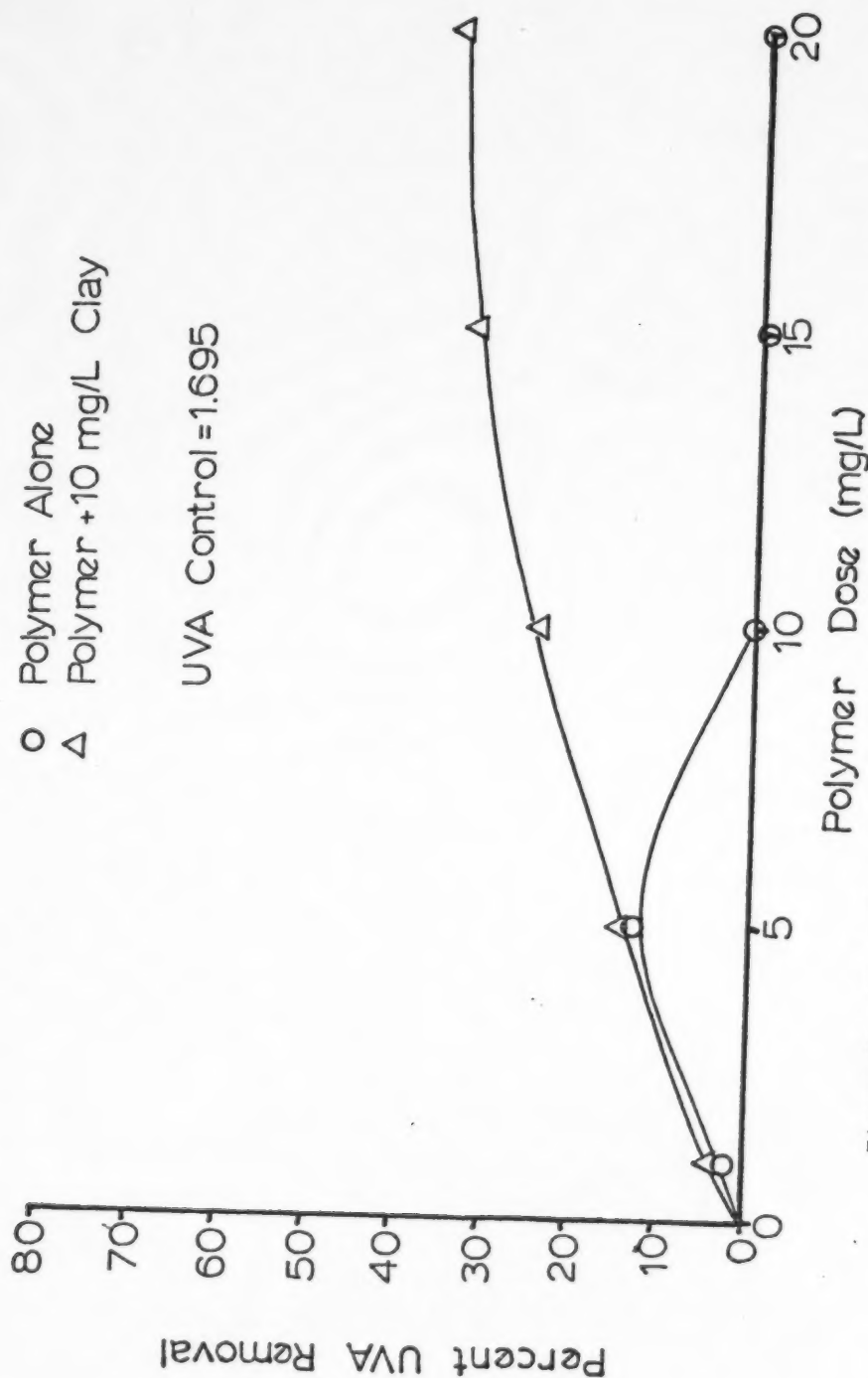


Figure 29. The effect of polymer dose (Nalco 8101) in conjunction with 10 mg/L Clay (Nalco 8153) on UVA removal.

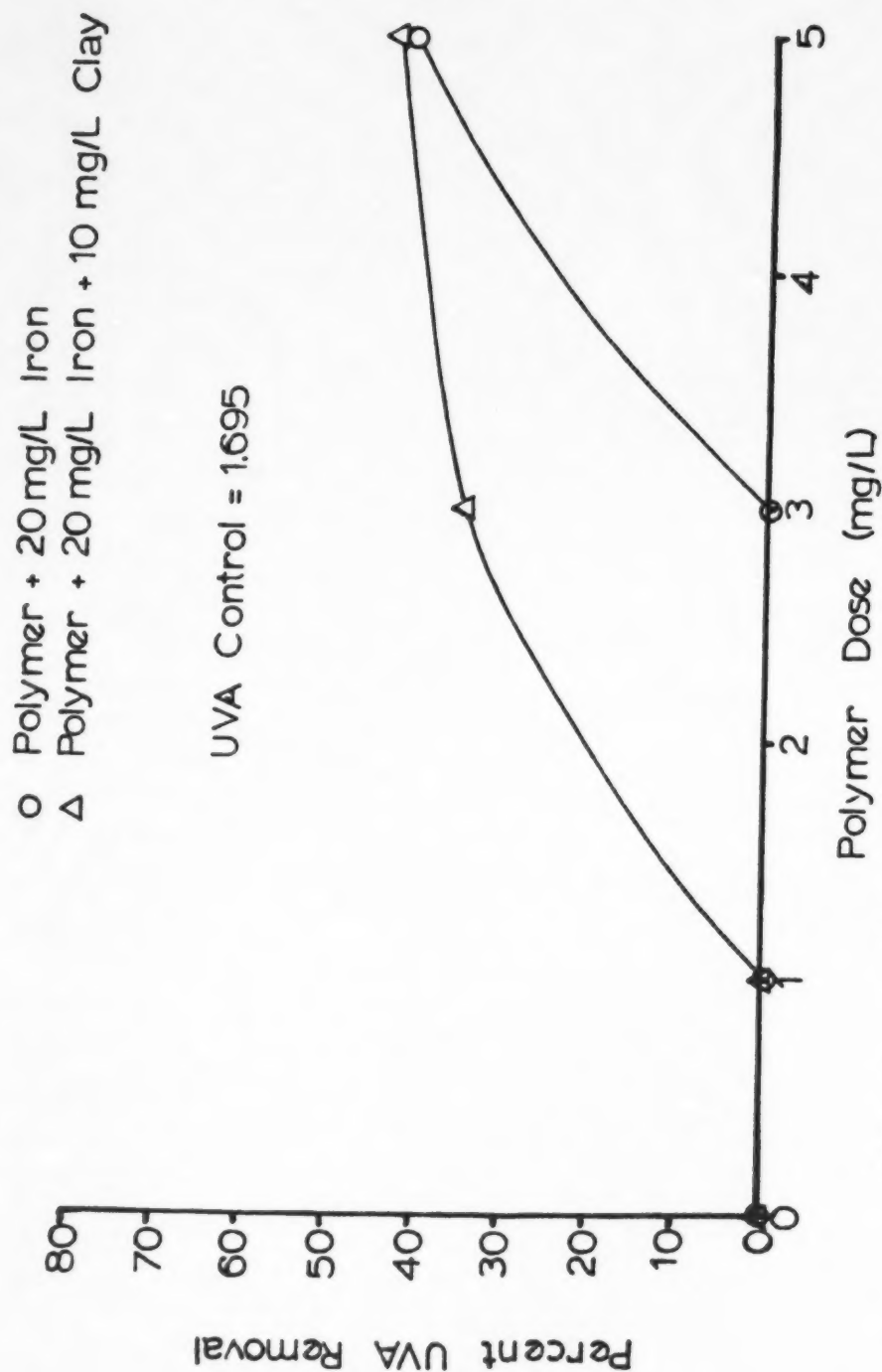


Figure 30. The effect of polymer dose (Nalco 8101) in conjunction with 10 mg/L clay (Nalco 8152) and 20 mg/L iron on UVA removal.

Activated Silica

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The use of activated silica in water treatment has been largely abandoned since the onset of synthetic polyelectrolytes, the reason being mainly that it is difficult to prepare. The exact nature of the silicon compounds formed during activation, and thus their role as coagulation-flocculation aids are largely unknown. In some cases, the polymer formed during activation may enter the aluminum hydroxide complex by replacing a hydroxide ion, thus being classified as a coagulant aid. In other cases the polymer may act as an anionic polymer, forming bridges between particles and thus behaving as a flocculation aid.

The activation of sodium silicate is accomplished by taking a concentrated sodium silicate solution at pH 12 and reducing the pH to approximately 9 so that the solution is over-saturated with respect to amorphous silica. Precipitate formation is arrested by diluting the solution after a selected period of aging. The variables in the activation process are: 1) initial sodium silicate concentration, 2) degree of acid neutralization, 3) the aging time, and 4) the final concentration of the diluted solution.

The two methods of preparation used were tested as recommended by Baylis (64) and Stumm et al. (65). The sodium silicate used was metasilicic acid, $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (Fisher Chemical Company) and the neutralizing agent was 30% H_2SO_4 .

The Baylis procedure of activation was as follows:

- 1) Initial concentration of sodium silicate = 1.5% as SiO_2 .
- 2) A 50 mL sample of the above was titrated with 30% H_2SO_4 to determine total alkalinity (pH-4.5). It took about 2.6 mL of acid as shown in Figure 31. The calculated alkalinity of the silicate stock solution was 24,300 mg/L as CaCO_3 .
- 3) Baylis suggested 2 methods of neutralizing the alkalinity. Both were tried.
 - a) Neutralizing 85% of total alkalinity.
 - b) Neutralize to a final alkalinity of 1200 mg/L as CaCO_3 .
- 4) The neutralized solutions were then aged for 30 minutes.
- 5) The aged solutions were then diluted to 2000 mg/L ($10^{-2.02}\text{M}$).

The procedure employed by Stumm was somewhat different. It consisted of titrating a $5 \times 10^{-3}\text{M}$ of sodium silicate at pH 13 with 30% H_2SO_4 to pH 6.0. The precipitated solution was allowed to age for 30 minutes and it was then diluted to 10^{-3}M .

The activated silica samples prepared following these procedures were tested as coagulant aids in conjunction with 20 mg/L of alum. The results with both activated silica samples indicated that no benefit was derived from their use. As an example, results in Figure 32 show activated silica had no impact upon UVA removal even when applied at doses as high as 20 mg/L.

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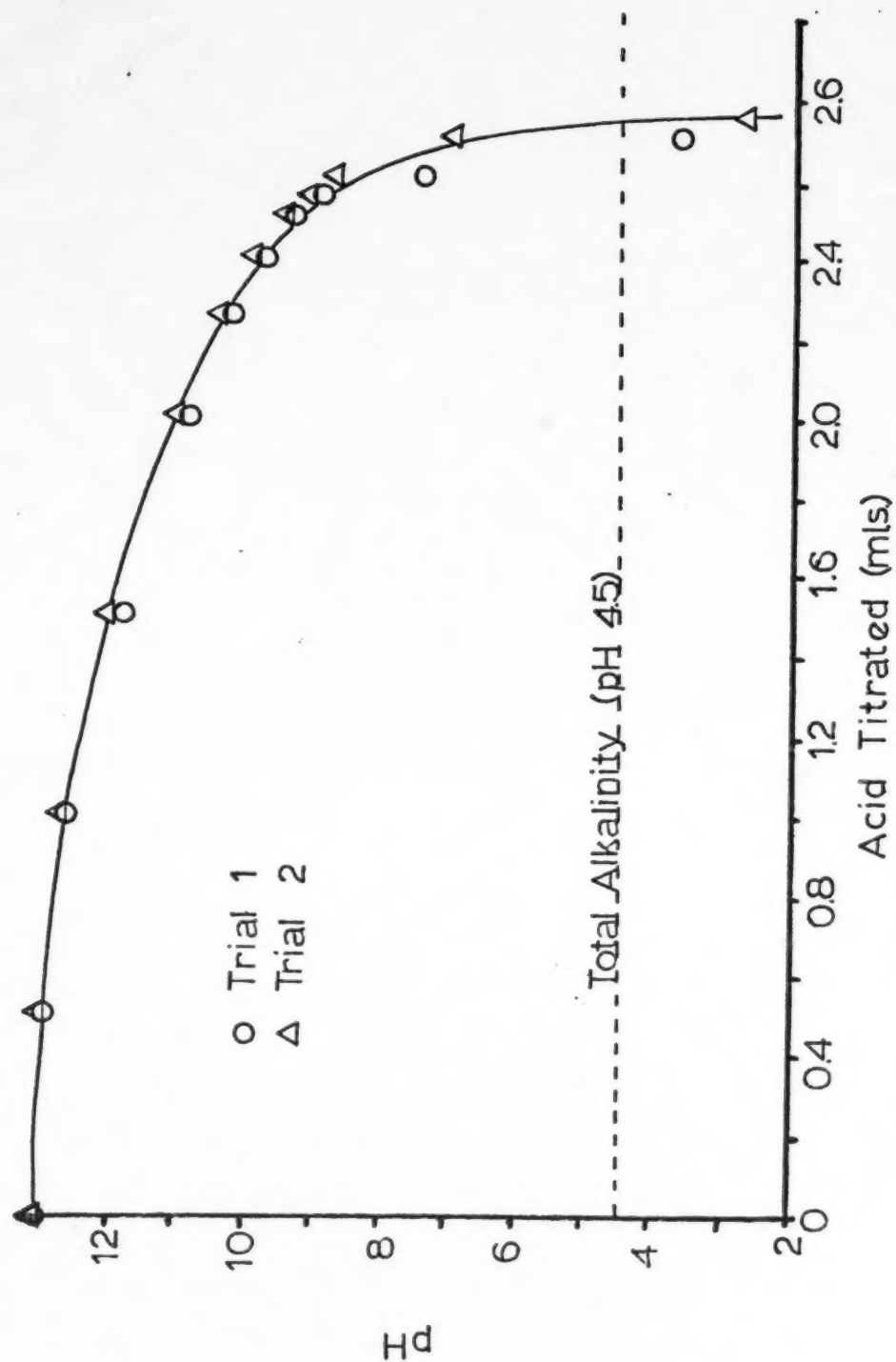


Figure 31. Titration of 50 mL $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ solution (50 g/L) with 9N H_2SO_4 to determine total alkalinity.

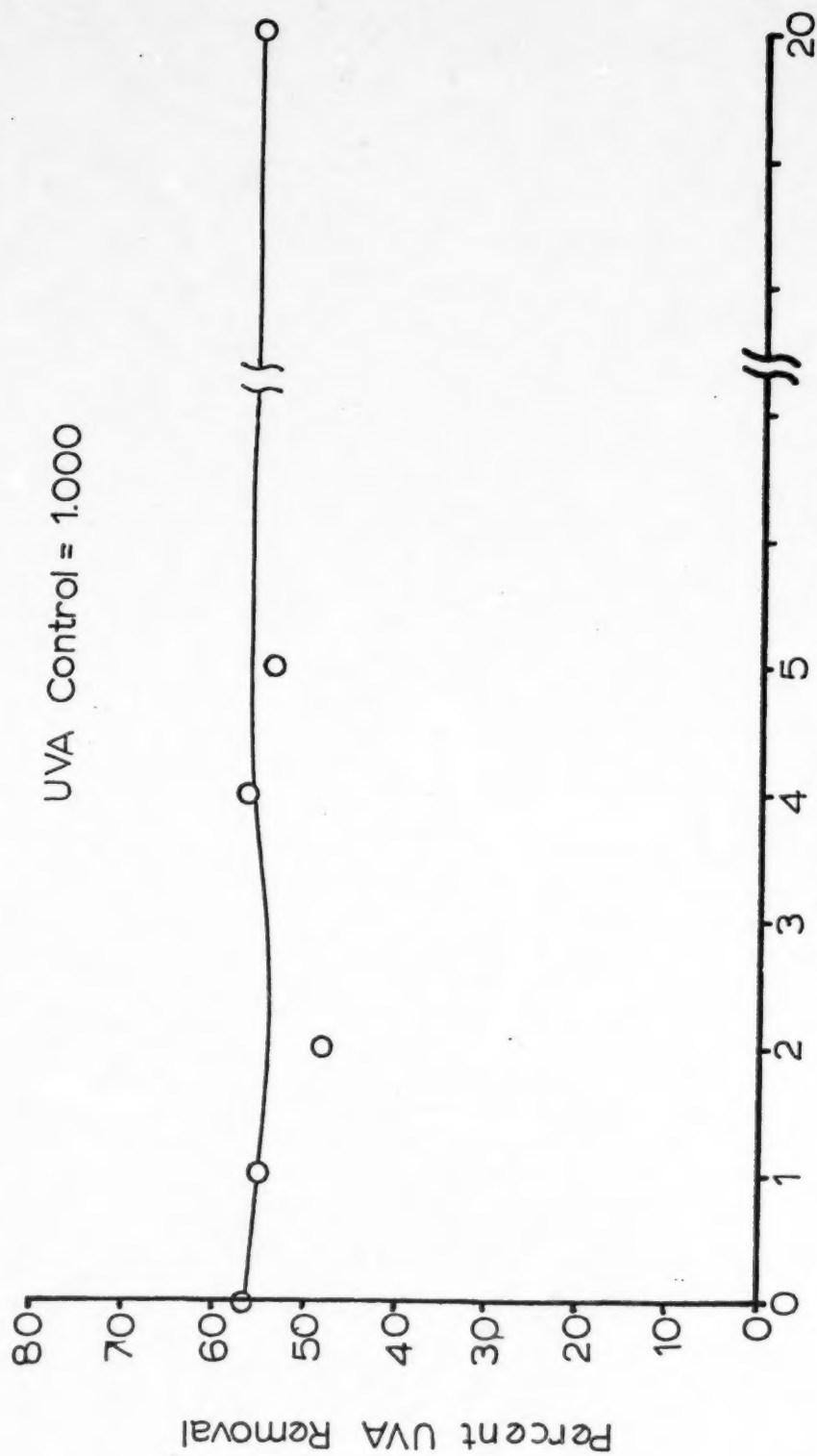


Figure 32. The effect of sodium silicate activated by the Stumm (65) method in conjunction with 20 mg/L alum on UVA REMOVAL.

Effect of Operational Variables

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Multi-Stage Coagulation

Field (14) and others have investigated the effect of operational variables on organics removals. From their results it may be concluded that mixing speed, slow mix time and order of chemical additions (i.e. timing of pH adjustment) had little effect on organics removals when using alum or ferric sulfate. Coagulant dose and pH were the most influential variables. In addition, Field (14) investigated the relative effectiveness of adding coagulant in stages compared to the conventional practice of adding a single coagulant dose. The results indicated that for coagulation at pH 5 there was no benefit to sequential addition of coagulant. However, Benedek (66) found that two-stage coagulation of water from the river Seine gave better organics removal than a single dose of coagulant. In his study, Benedek did not control pH as Field did. It should be recognized there may be significant differences in the character of surface water organics which could perhaps account for differences in observed removal behavior. However, the impact of solution pH on organics removal behavior is so significant that it was considered more likely that the difference in behavior was attributable to the maintenance of different pH conditions in the two studies. Recent studies by Jekel (67) tend to support this view. These investigators identified changes in the mechanism of organics removal at different pH values. At neutral pH values (7-9) adsorption was thought to be the predominant mechanism of removal, whereas at more acidic pH values (4-6) complexation/precipitation predominated.

In light of these observations and the changes in the principal removal mechanisms at different pH values it was apparent that the staged addition of coagulant may be beneficial at higher operating pH values. A study was, therefore, conducted to evaluate the impact of sequential coagulant addition at different pH values.

The procedure employed is presented schematically in Figure 33. An 800 mL sample of river water was coagulated with 3 coagulant additions of 25, 25 and 50 mg/L. Each addition was made with a 5 second rapid mix. This was followed by 30 min. flocculation, 1 hour of sedimentation and filtration to remove the flocculated solids. A portion of the filtrate was separated for analysis and the remaining sample was subjected to additional coagulation. The results of this study were compared to a control coagulation study on the same sample in which the coagulant was added in a single addition of 100 mg/L. The study was duplicated at pH 5, 7 and 9.

The results are reported in Figures 34 and 35 in summary form. The removals obtained for different coagulant doses and pH values are presented as bars. If a benefit were observed with sequential addition, the bars are extended with a cross hatched bar. As Figure 34 indicates, a slight benefit was observed for sequential addition of coagulant at pH 7 and pH 9; however, at pH 5 no benefit was observed and the performance of single and multi-stage coagulation was identified. The extent of the benefit observed with multi-stage coagulation was not great and the increased effectiveness of the coagulant must be weighed against the increased capital cost required for

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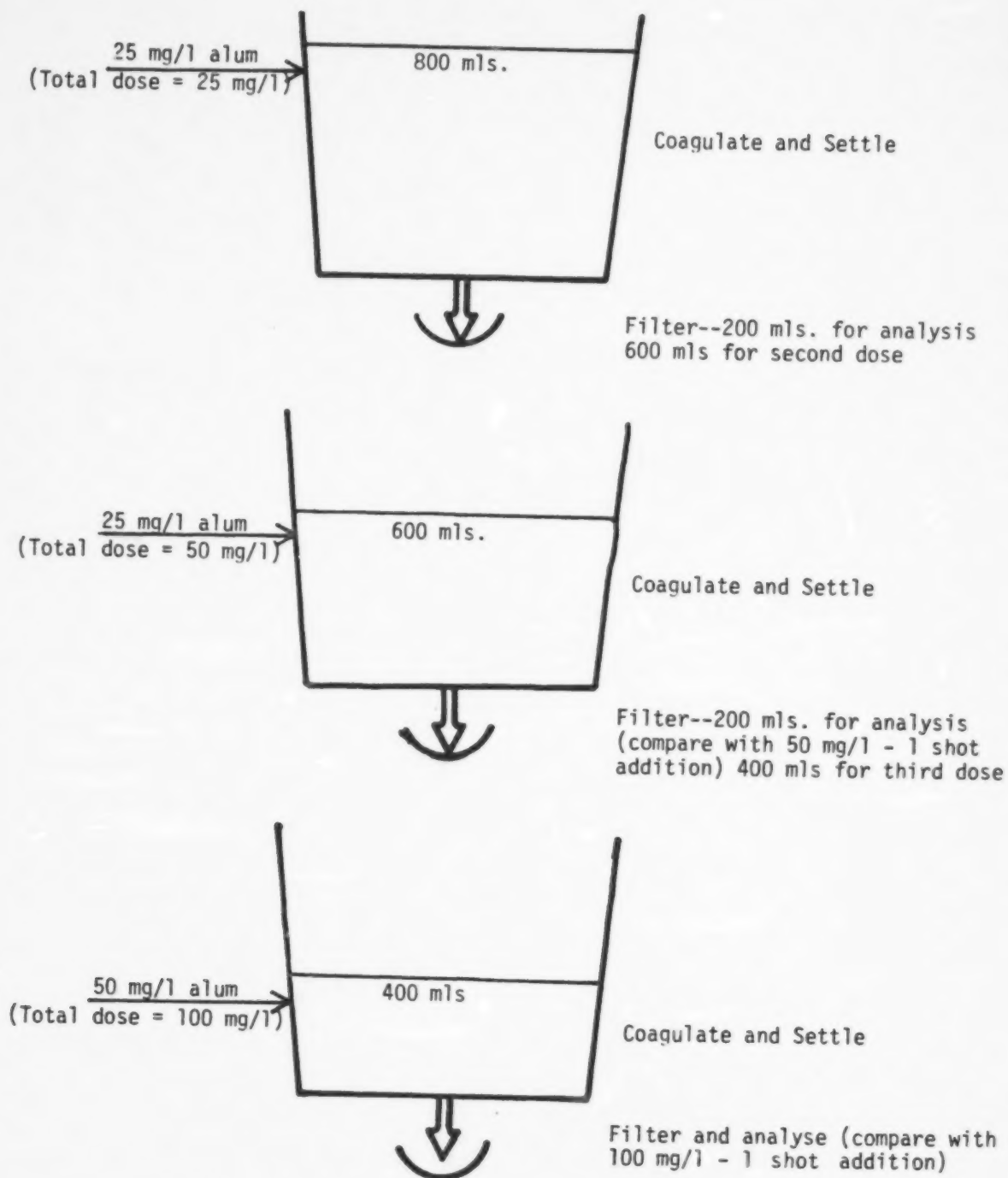


Figure 33. Procedure for sequential dose test (pH 5,7,9)

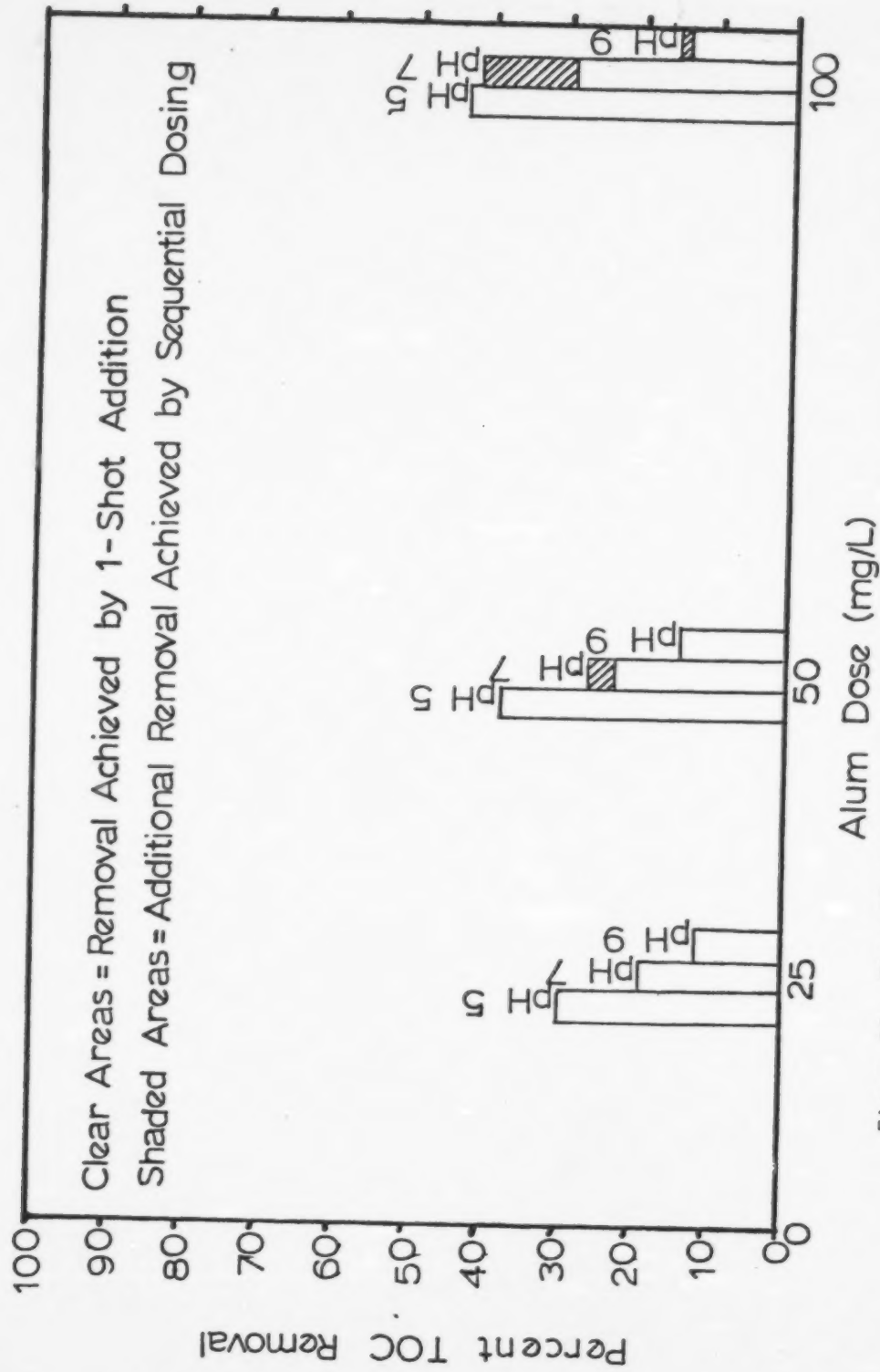


Figure 34. The effect of sequential dosing of alum on TOC removal.
 TOC control = 7.7 mg/L.

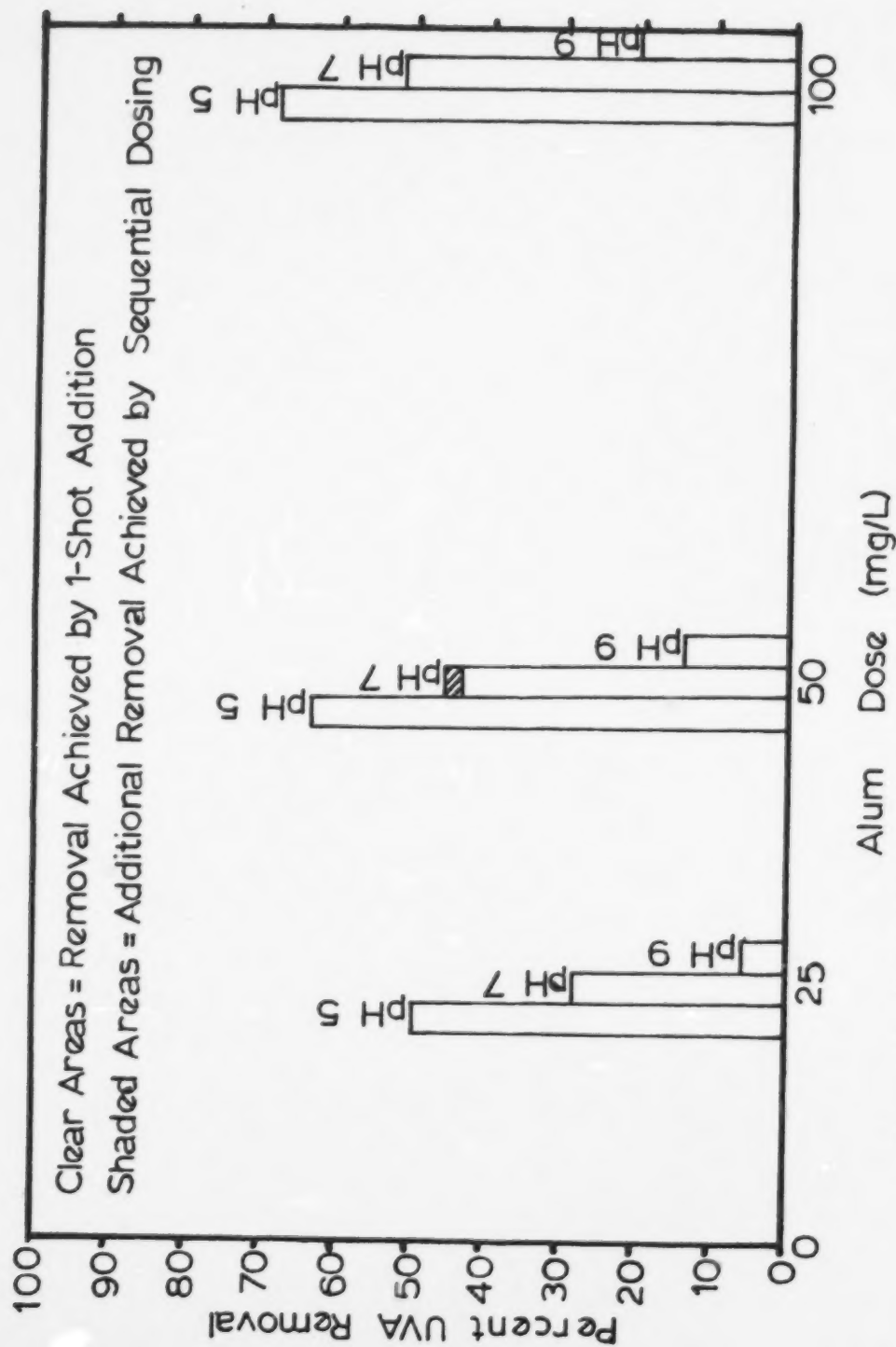


Figure 35. The effect of sequential dosing of alum on UVA removal.
UVA control = 0.772.

separation of first-stage flocculated solids.

Coagulant Modification

Several investigators have reported beneficial effects as a result of coagulant aging.

A study was conducted to evaluate the performance of pre-precipitated alum and aged $Al(OH)_3$ as compared to the performance of freshly prepared alum that was normally applied. An alum stock solution (50 mg/L) was prepared and neutralized to pH 7.0 before addition to river water samples. The neutralized suspension was tested directly and it was also tested after being aged. Two aged alum suspensions were prepared: one was prepared by storing the neutralized alum suspension for 7 days at room temperature; for the second solution, the aging process was accelerated by elevating the temperature to 60°C for eight hours. In each of these tests care was taken to ensure that the hydroxide precipitate in the neutralized alum stock solution was constantly suspended, making the solution uniform. Each test was conducted at a coagulation pH of 5 and 7, and covered a dose range of 0 to 100 mg/L. The results for the unmodified alum control and the neutralized alum aged at 60°C for 8 hours are presented in Figure 36. The data indicated that the pre-neutralized alum performed more poorly for organics removal than the unmodified alum. The other modified alum samples that were prepared also gave poorer removal performance than the control and there was no benefit to be derived from these modification procedures.

Reversibility of Organics Removal by Alum

A series of tests were performed to test the reversibility of organics removal by alum. Initial tests were conducted to determine organics removal as a function of alum dose and pH of coagulation. Alum doses of 20, 40, 60, 80 and 100 mg/L were selected for coagulation at pH values of 5, 6, 7, 8 and 9. As expected, (2,3,4,5) organics removal was strongly dependent on pH and dose. From this data alum doses of 20, 60 and 100 mg/L (representing a low, medium and high dose) were chosen for the reversibility study.

For each dose, the following procedure was employed:

- A. 1) Coagulate 900 mls at pH 5, slow mix for 30 min.
- 2)* Withdraw 300 mL
 - 150 mL - settle, filter, analyze
 - **150 mL - kinetic study
- 3) Adjust pH of remaining 600 mL to pH 7, slow mix for 30 min.
- 4) Withdraw 300 mL
 - 150 mL - settle, filter, analyze
 - 150 mL - kinetic study

*When sample was withdrawn, care was taken to ensure a homogeneous sludge/water ratio using a glass stirring rod to keep the sludge suspended.

**Each sample was split, half of it being analyzed after 30 min. of mixing, 1 hour of settling and filtration, the other half was placed on a rotary shaker for 24 hours, after which it was settled, filtered and analyzed.

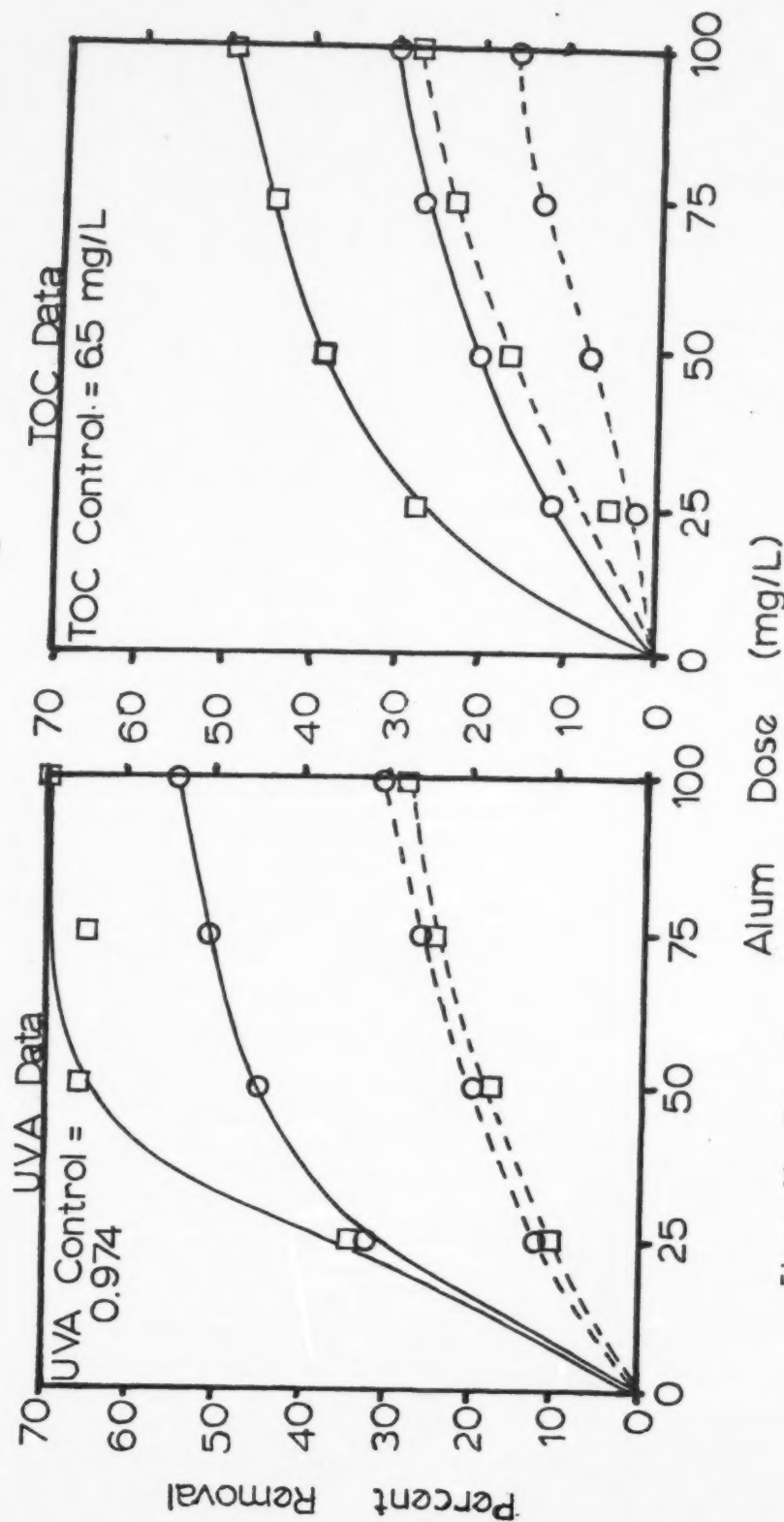


Figure 36. The effect of alum premodification on organics removal from Mississippi River water.
 □ — pH 5
 ○ — pH 7
 — Unmodified alum
 --- Neutralized alum aged at 60°C for 8 hrs.

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- 5) Adjust pH of remaining 300 mL to pH 9, slow mix for 30 min.
- 6) Stop slow mix
150 mL - settle, filter, analyze
150 mL - kinetic study

- B. Identical to part A, but instead of adjusting the pH from 5 to 7 to 9, adjust from 9 to 7 to 5.

The UVA and TOC results for each of the alum doses are presented in Figures 37 through 42. In these figures the solid line represents the expected removal for the given dose as a function of pH. The upper line (arrows point right) traces removal as the pH of the sample was modified from pH 5 to 7 to 9. The lower line (arrows pointing left) traces removal performance as the pH of the sample was modified from pH 9 to 7 to 5. In each case, as the pH was raised from 5 to 9, the sludge released organics back to solution, and as the pH was lowered from 9 to 5, soluble organic matter became incorporated in the sludge. Also note that a sample coagulated at pH 5, then raised to pH 9 always resulted in slightly higher removals than a sample coagulated originally at pH 9. Conversely, a sample coagulated at pH 9 then lowered to pH 5 never quite removed as much as the sample coagulated at pH 5 originally. The data indicated that reversibility, although substantial, was not quite complete. Analysis of the samples that were shaken for 24 hours indicated that no additional organic removal occurred and the incomplete reversibility could not be attributed to a simple kinetic effect. It is likely that kinetic intermediate hydrolysis products of alum play a role in organics removal and the formation of these products is dose and pH dependent. Changing solution pH following coagulation will alter the charge characteristics of the organic compounds and also the equilibrium speciation of the alum. However, it will never duplicate the formation of hydrolysis products that may be formed as kinetic intermediates at a given pH. For example, polycationic polymeric intermediates are known to form during coagulation under slightly acidic pH values (5-6). At pH 9 the formation of these intermediates is greatly reduced.

The equilibrium nature of organics removal was also tested by diluting a coagulated river water sample with an equal volume of river water. If the organics removal process was reversible, this procedure should yield organics removal levels in the mixture equivalent to half the original coagulant dose.

Three 800 mL samples of water were coagulated with 40, 80 and 120 mg/L of alum. After 30 minutes of slow mixing, 400 mL were removed from each well stirred sample and replaced with 400 mL river water. The mixtures were then reflocculated for 30 minutes, settled, filtered and analyzed. This test was performed at pH 5, 7 and 9. The results are shown in Figures 43 and 44. The solid line shows expected removals for each pH and dose if the removal process was reversible. The triangles represent removals achieved by doubling the solution volume (halving effective dose). For example, a triangle at 40 mg/L alum represents removal achieved by doubling the solution volume after coagulation at 80 mg/L. As in the reversibility studies reported above, it appeared that organics removal was partially reversible.

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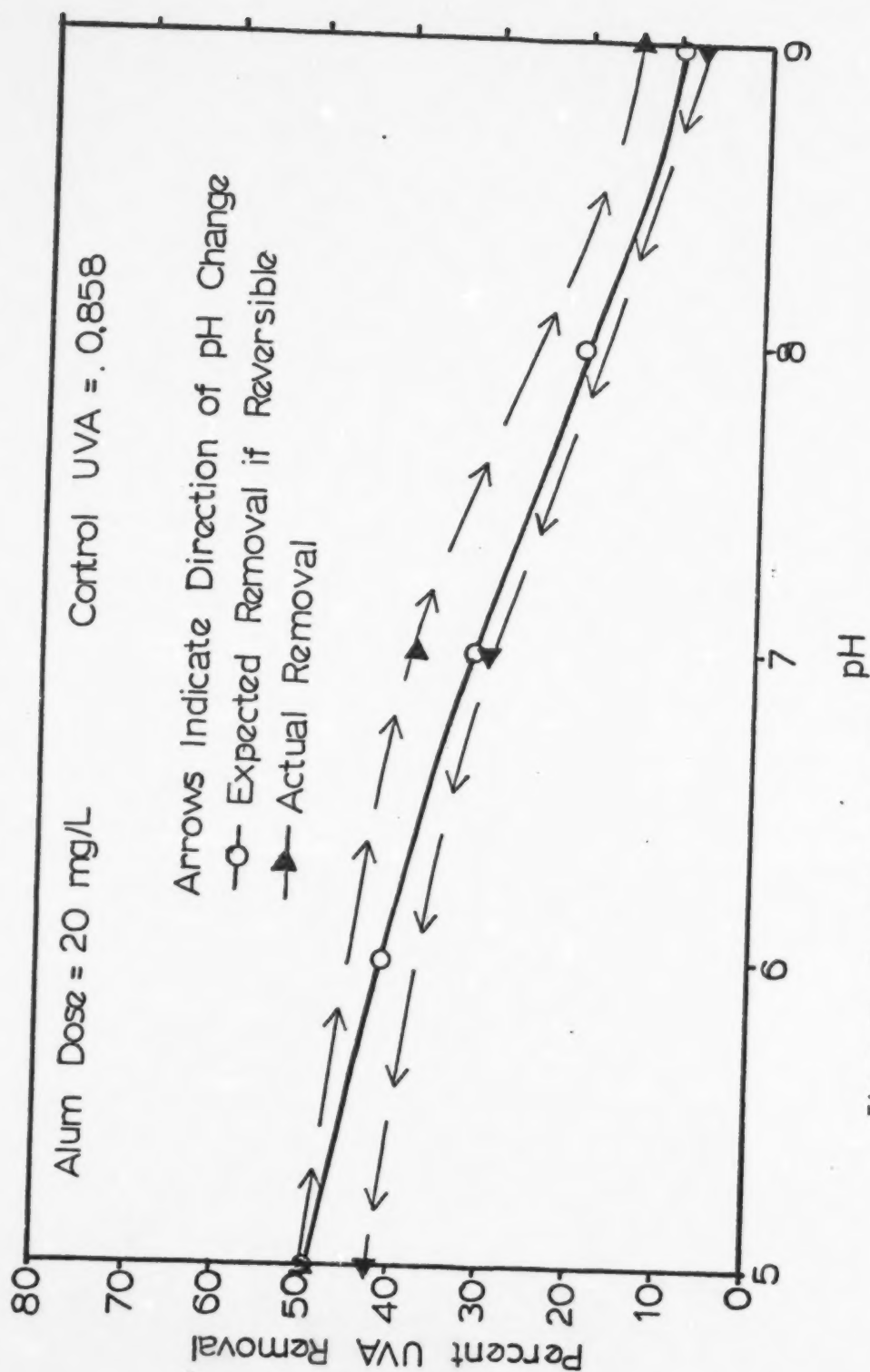


Figure 37. Reversibility of UVA removal by pH change for 20 mg/L alum

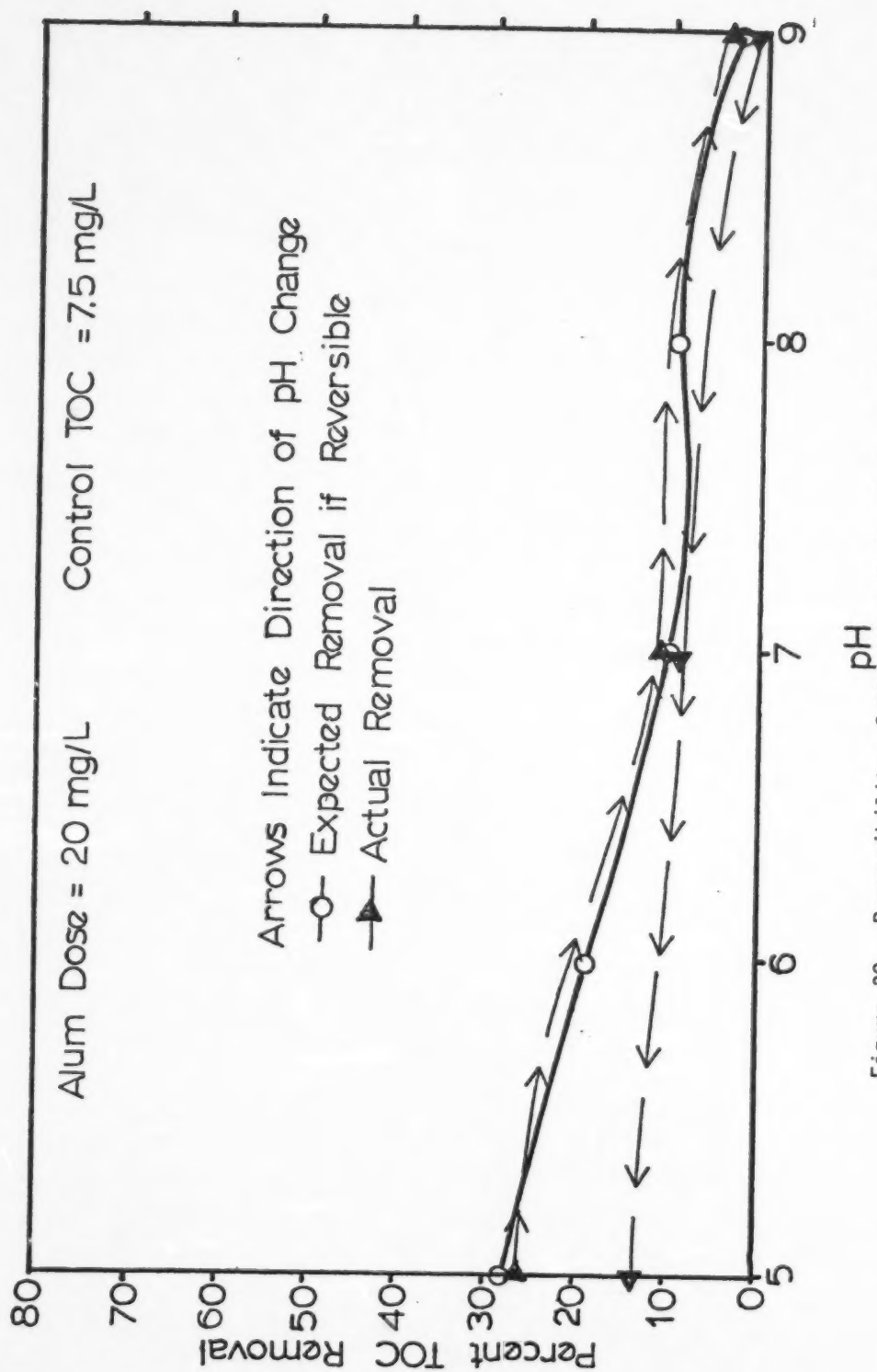


Figure 39. Reversibility of TOC removal by pH change for 20 mg/L alum.

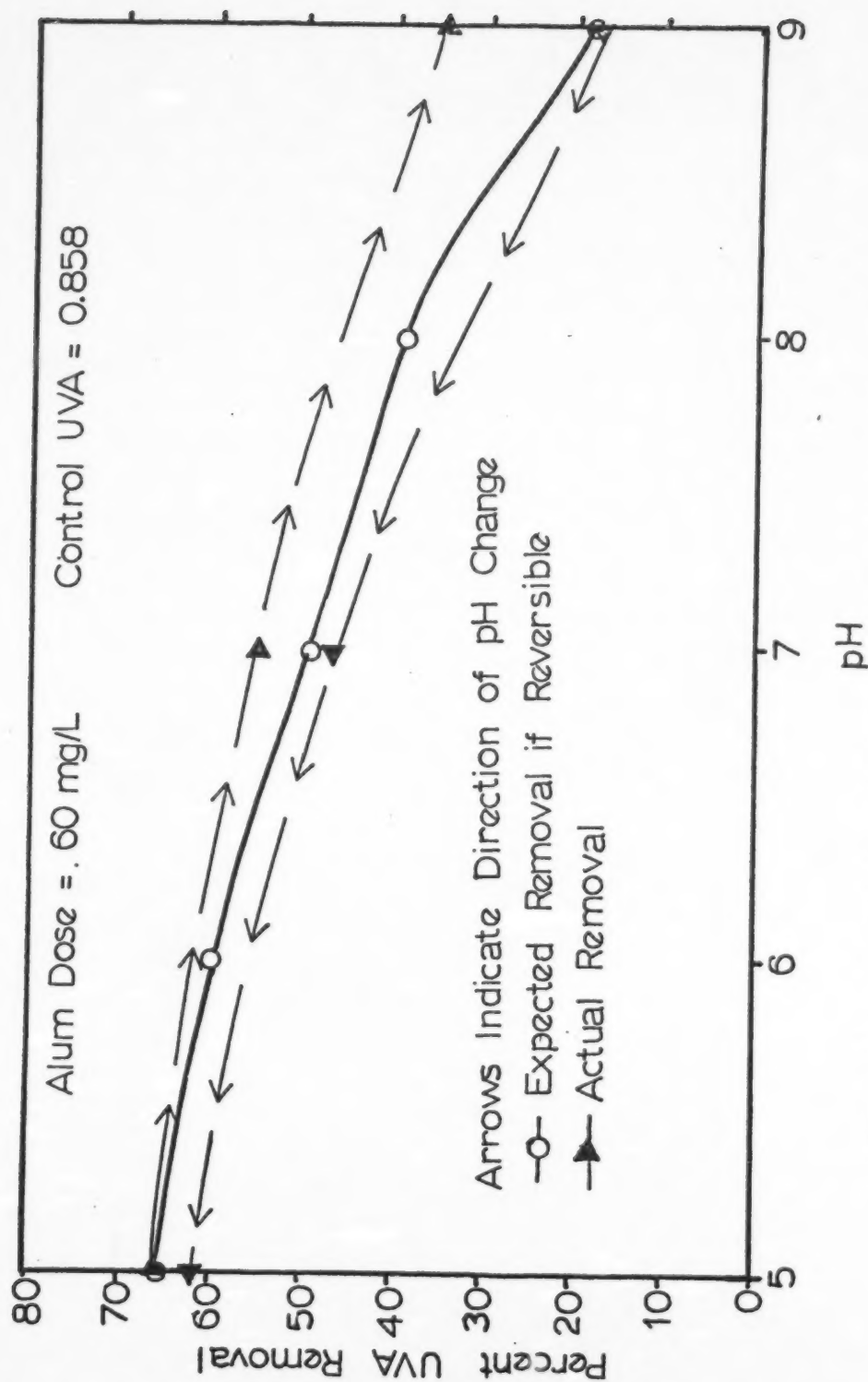


Figure 39. Reversibility of UVA removal by pH change for 60 mg/L alum.

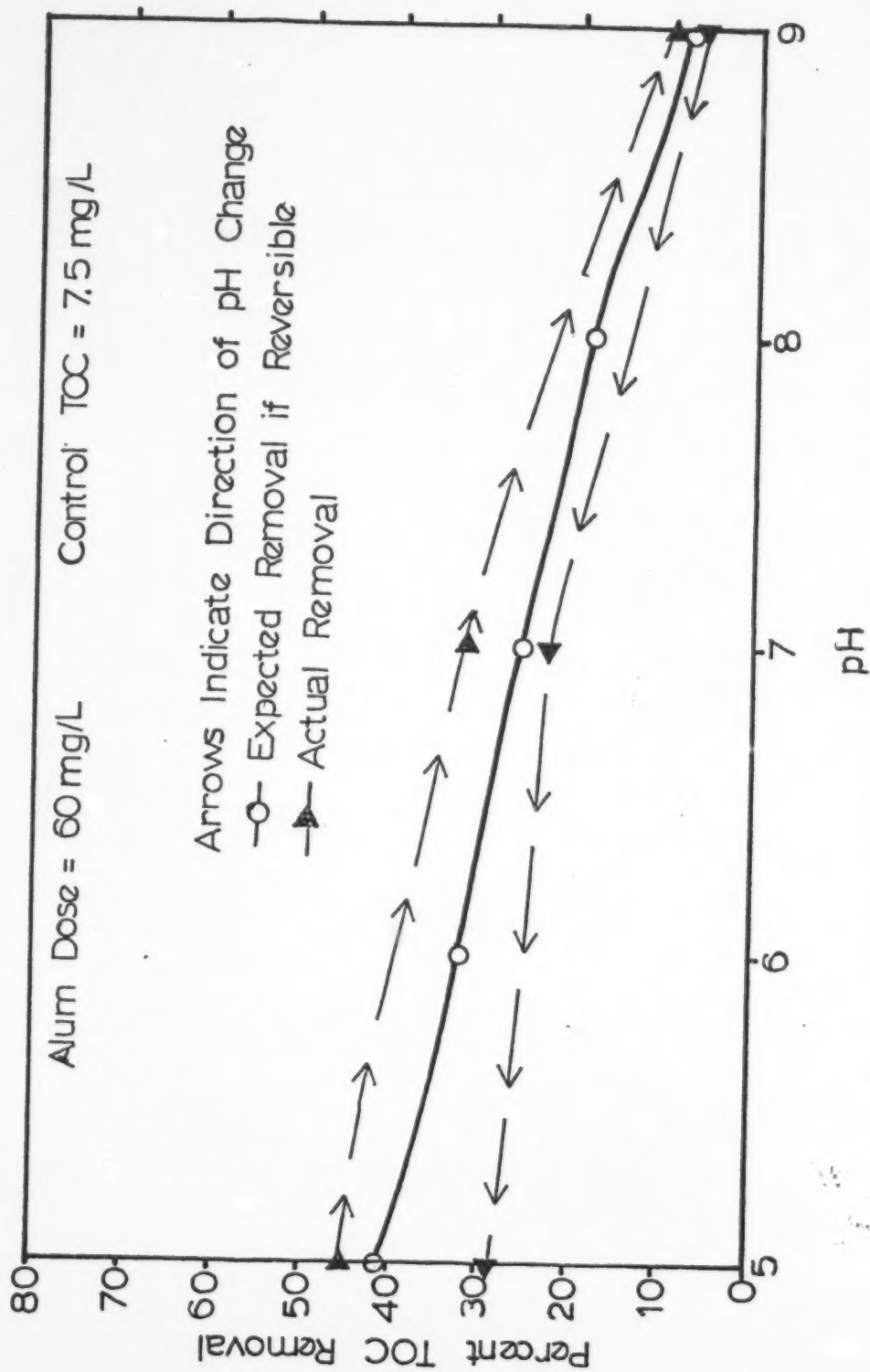


Figure 40. Reversibility of TOC removal by pH change for 60 mg/L alum.

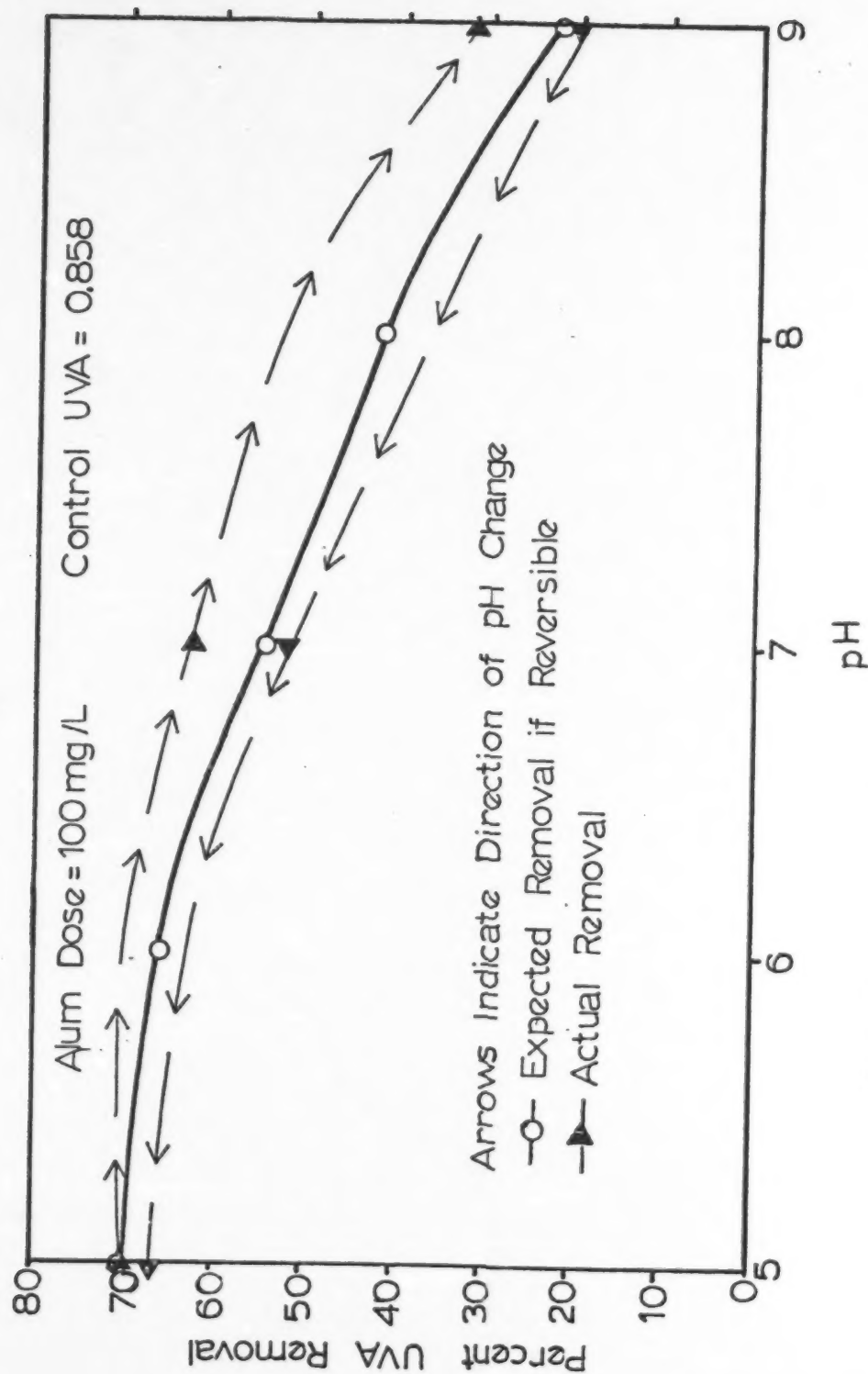


Figure 41. Reversibility of UVA removal by pH change for 100 mg/L alum.

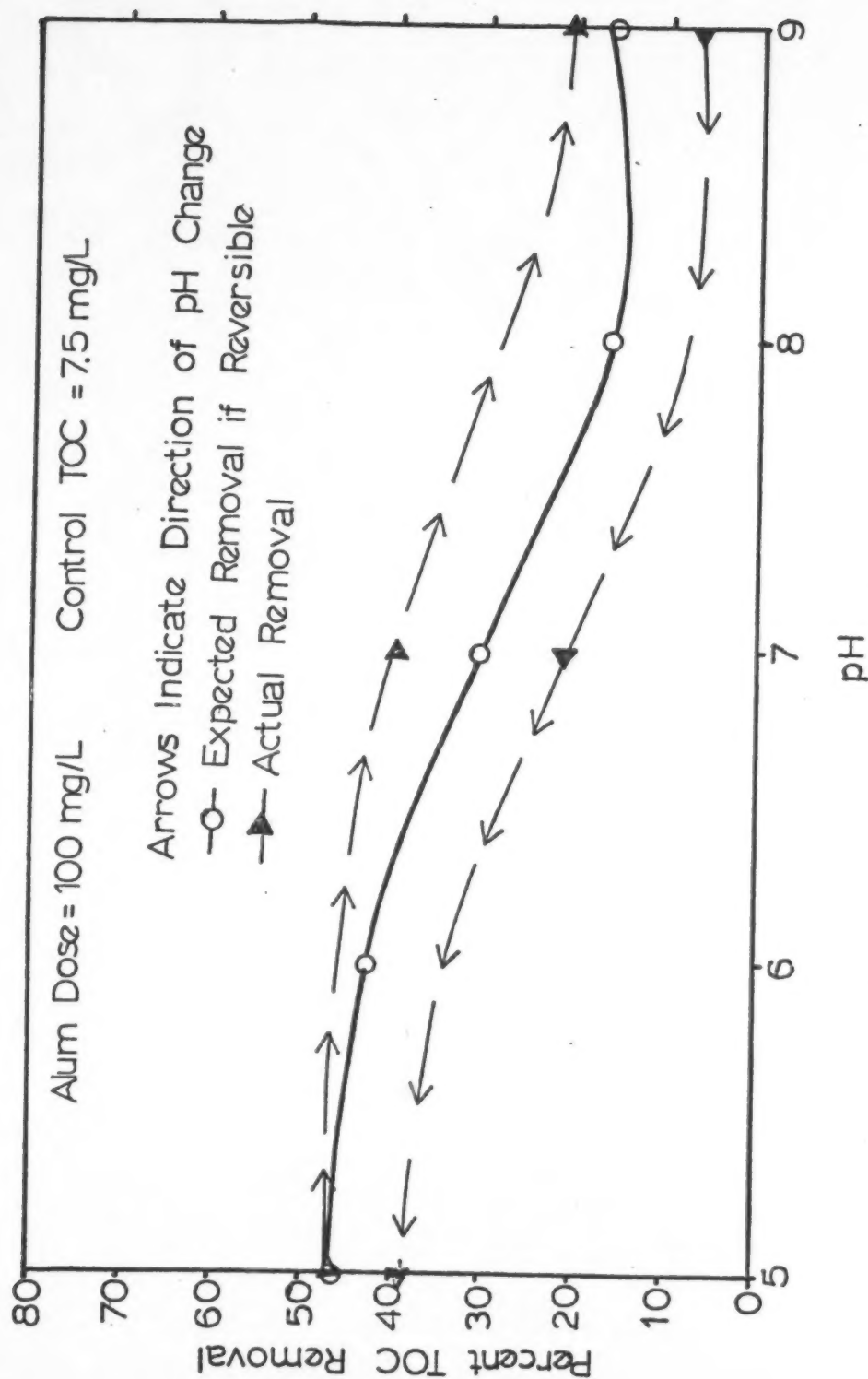


Figure 42: Reversibility of TOC removal by pH change for 100 mg/L alum.

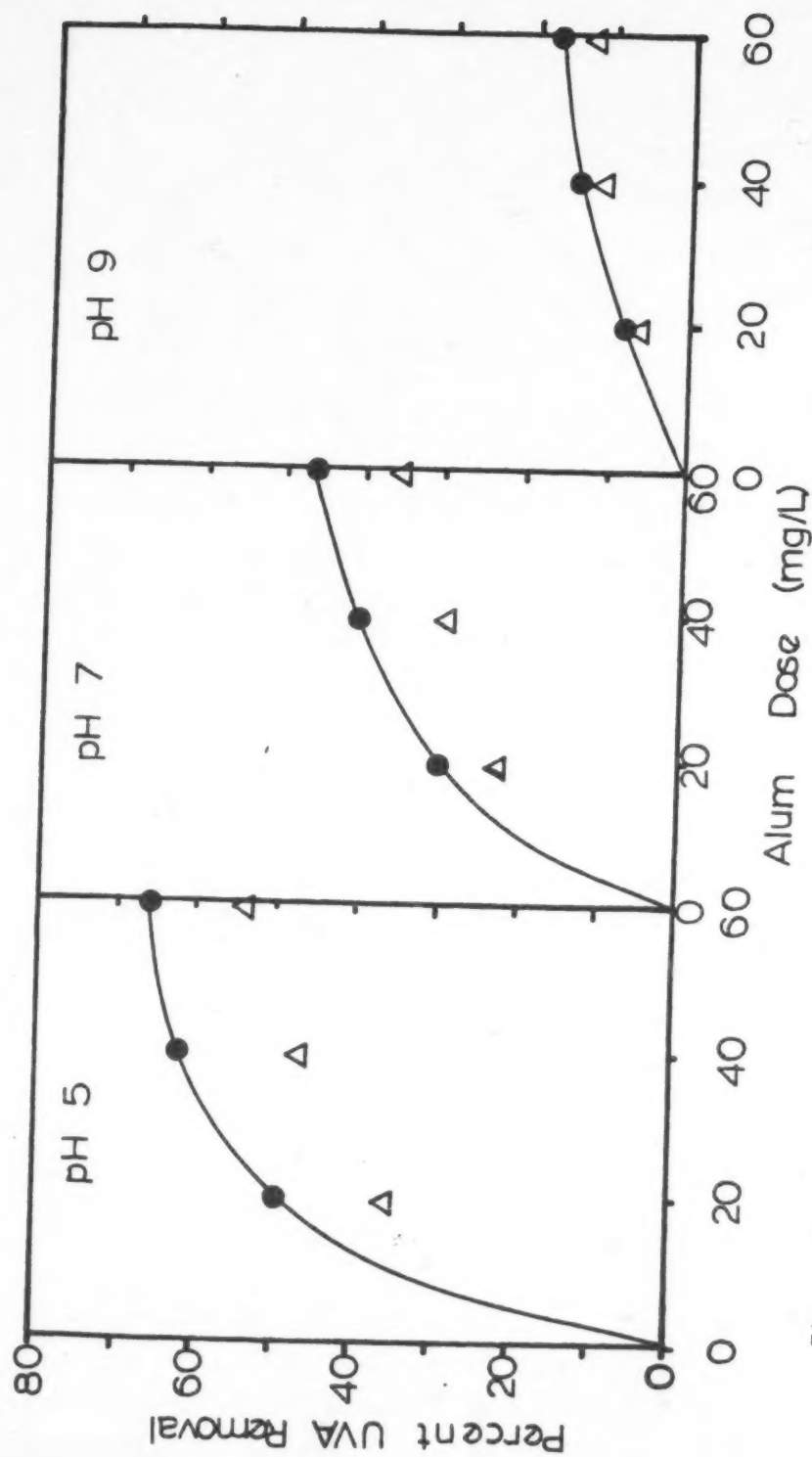


Figure 43. Extent of UVA removal following dilution with Mississippi River water. ● Expected removal if reversible Δ actual removal. Control UVA = 0.807

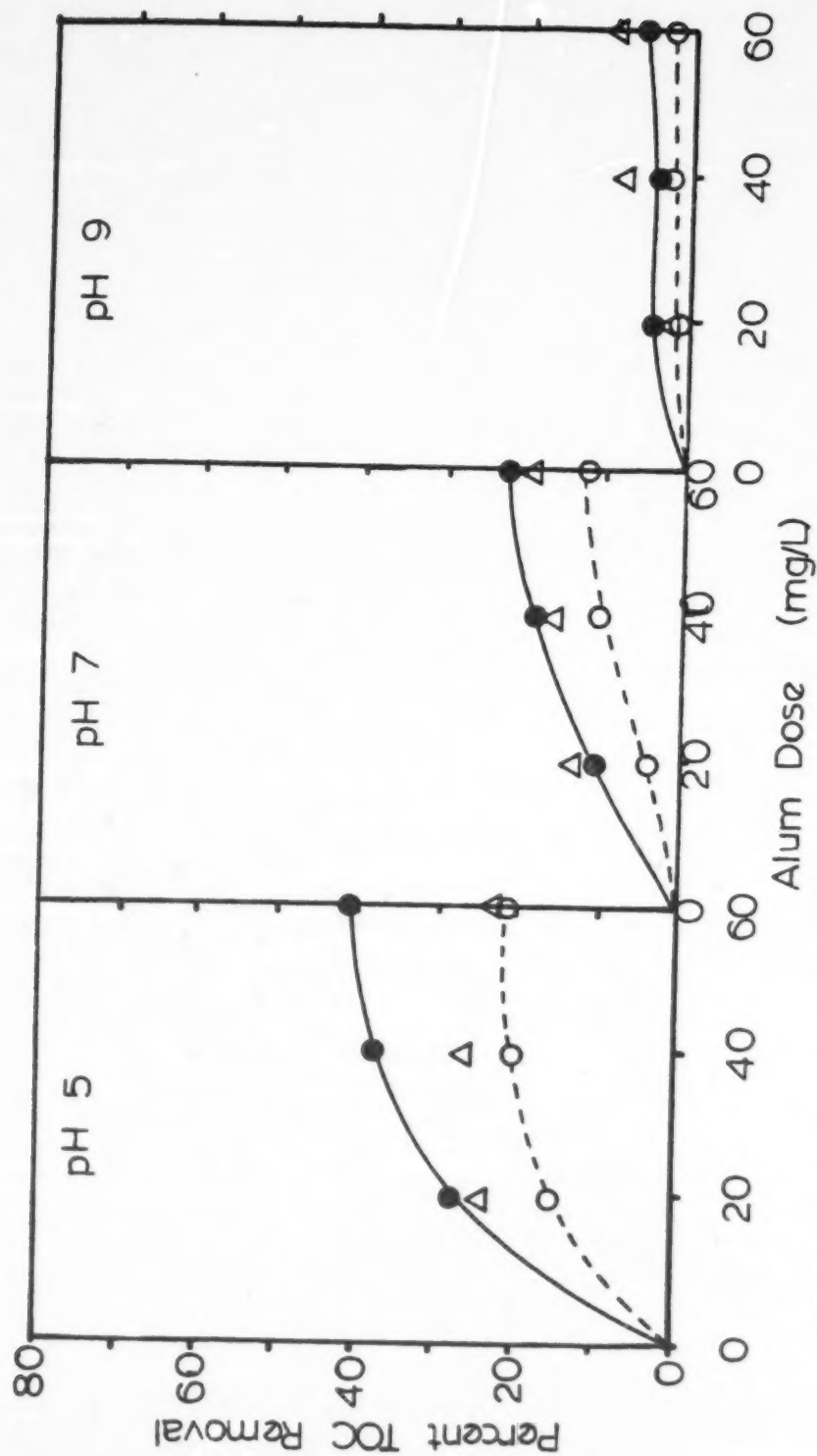


Figure 44. Extent of TOC removal following dilution with Mississippi River water. (Control TOC = 7.7 mg/L). 0 - expected removal if reversible; Δ - actual removal

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Field (14) obtained similar results for reversibility for a sludge produced by coagulating river water with a 100 mg/L alum dose. By separating the sludge and diluting it with organic free deionized water to 500 mL, and flocculating, settling and filtering the sample, he found a significant release of organics to the solution phase. The alum dosages were applied at pH levels ranging from 4 to 9 and the pH of the deionized water was adjusted to the pH of the solution from which the sludge was separated. The sludge released up to 25% of its organic content into solution between pH 5 and 6.

The reversible nature of organics removal by alum is significant and should be recognized by design engineers. For example, sludge handling or conditioning procedures that may elevate the pH of an alum sludge generated in the coagulation of a colored water may cause the water removed in the thickening or dewatering processes to be highly colored.

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SOFTENING STUDIES

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A large proportion of water treatment facilities in the USA chemically soften their source waters to reduce the hardness to acceptable levels, usually between 80 and 100 mg/L as CaCO_3 . The softening process involves lime addition to elevate the pH and precipitate calcium carbonate and magnesium hydroxide. In waters where the natural alkalinity is low soda-ash (Na_2CO_3) may also be added to provide sufficient carbonate ions for the desired level of calcium removal.

It is obvious that the softening process improves the quality of the water and removes some of the naturally-occurring organic content of the water. The process reduces the turbidity and the color of the source water. The organic compounds contributing to color are removed in the precipitation process by processes that may include co-precipitation, absorption, enmeshment, etc. Although there is not a lot of flexibility in the operation of a softening process, the desired final hardness is not rigidly fixed and may be varied slightly if there is a good economic reason to justify it. In addition, the use of coagulants and polymers may allow a target hardness to be achieved with slightly lower chemical doses (57) and may also influence organic removal in the softening process.

Very little research has been conducted to evaluate organics removal by softening, and essentially no research has been conducted to identify the influence of operating variables upon organics removal and the character of organics removed by softening. This section reports the results of batch studies conducted to evaluate the impact of softening under different conditions on the simultaneous removal of hardness and organic content. Because of the excellent correlations between TOC and UVA and TTHMFP, UVA was employed as a monitor of organics removal effectiveness in many of these tests. Column studies on softening were also conducted but these are reported in Section 8. The character of organics removed by softening was evaluated using a variety of organic fractionation techniques and the results are presented in Section 7 of this report.

EXPERIMENTAL RESULTS

1. The effect of lime addition as a slurry vs. a powder.

Two separate jar tests were conducted to compare the removal of organics when lime was added as a slurry to that obtained when lime was added as a dry powder. Also examined in these tests was the effect lime dose had on organic removal. This experiment was designed for the most part to determine what experimental conditions should be used in future tests, but it was also felt that the results could have practical significance for the operation of water treatment plants.

The lime used in this study was reagent grade calcium hydroxide. A Mettler 15 analytical balance was used to weigh out the dry lime powder.

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Precise lime addition as a slurry was accomplished by pipetting the appropriate amount of a well-stirred lime stock solution.

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The tests indicated there was little difference in performance as a result of the way in which lime was added. The ultraviolet absorbance (UVA) measurements on the treated water samples indicated almost identical behavior as shown in Figure 45. Concentrations in the river water sample used were not known so a range of lime dosages was examined based on known yearly fluctuations in hardness levels. As the figure indicates, an essentially linear decrease in UVA was observed with increasing lime dose up to a treatment of about 200 mg/L as CaCO_3 at which point the removal seemed to plateau at approximately 60% removal. Later measurements indicated that the raw water treated was very low in hardness (108 mg/L as CaCO_3 total hardness). In practice this water would require a lime dose of only 70-80 mg/L as CaCO_3 . From figure 45 it is apparent only 20% UVA removal would occur at this stoichiometric lime dose.

An additional study was conducted on a different river water sample having an initial hardness of 188 mg/L as CaCO_3 . The impact of lime dose (added as a powder) indicated that organics removal could be improved by increasing the lime dose beyond the 210 mg/L calculated stoichiometric dose for a final hardness of 80 mg/L. The result is shown in Figure 46 and a plot of organics removal versus final pH for this water sample is presented in Figure 47.

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Because organics removal was not significantly affected by the technique of lime addition in later batch studies lime was added as a dry powder. The results also indicated that organics removal increased as the final pH was increased by larger lime doses. It was noted that lime doses in excess of the stoichiometric amount required for the softening objective (80 mg/L hardness) gave improved organics removals.

2. Kinetics of Organics Removal During Lime Softening

In the softening studies conducted above, the river water was in contact with the precipitated solids for 2 hours at the most and there was some question as to whether removal was complete after this short contact period, so a study was designed to measure the kinetics of organics removal during excess lime treatment.

A 10 liter river water sample with a hardness of 189 mg/L was treated with a lime addition of 115 mg/L as CaCO_3 . Dry lime was added during a 30-second rapid mix and the water was then flocculated at 30 rpm. Grab samples (100 mL) were taken from the mixed suspension and immediately filtered with prewashed glass fiber filters. The filtered water was then examined for organic content by ultraviolet absorbance measurements. Measurements were made as a function of time for the first four hours and then a 150 mL sample of slurry was taken from the flocculation tank and placed in an erlenmeyer flask. This sample was shaken for an additional 20 hours on a rotating shaker and filtered and tested in the manner of previous samples.

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The results of this study are summarized in Figure 48. It was apparent

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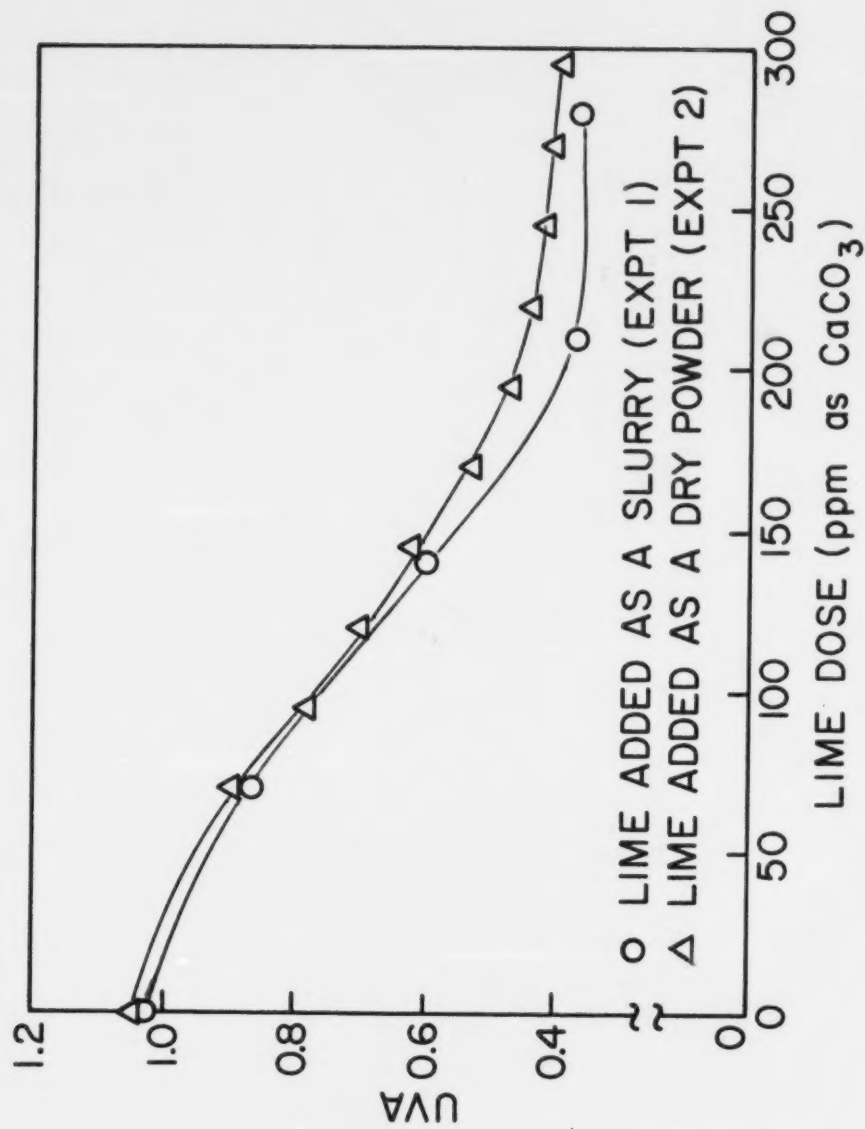


Figure 45. The effect of lime dose on organics (UVA) removal from Mississippi River water (dry powder vs. slurry).

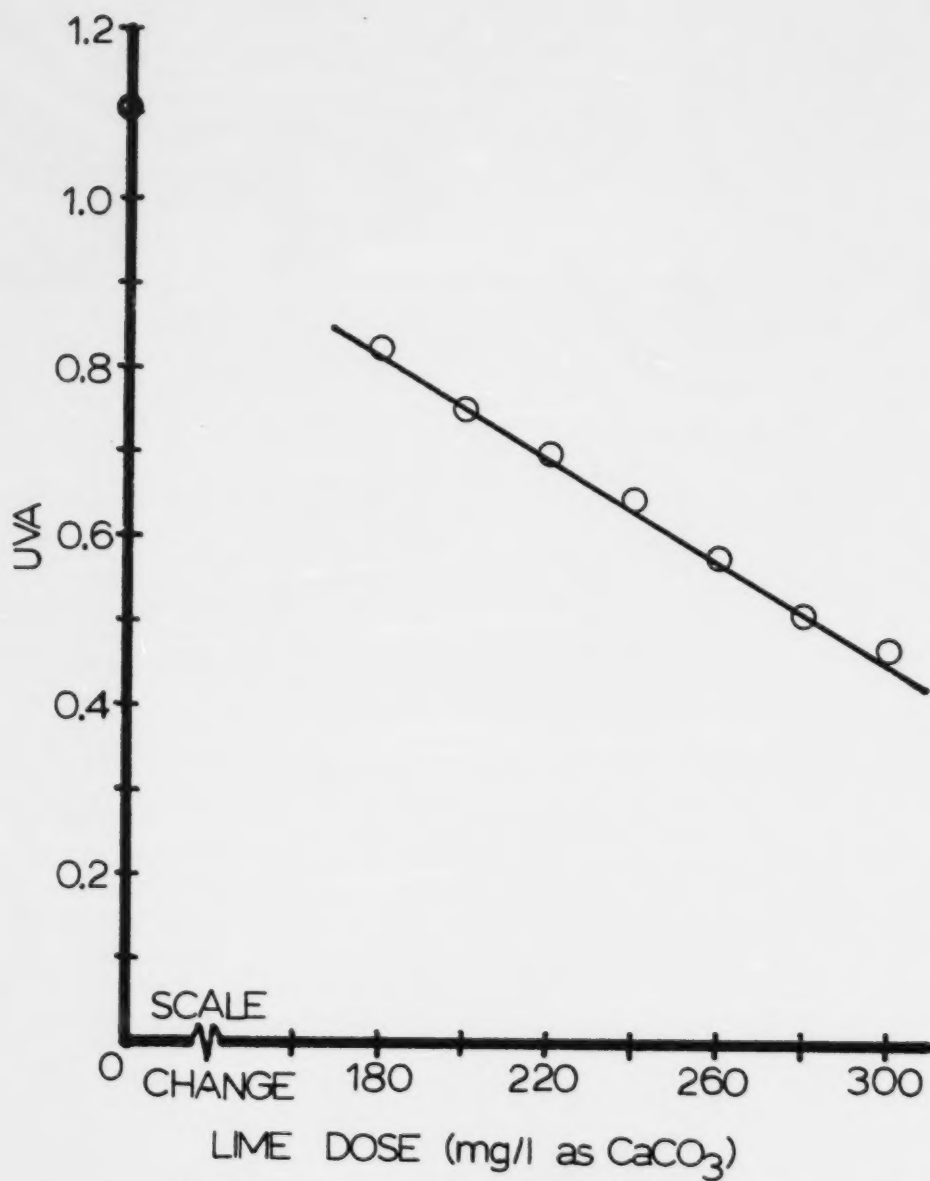


Figure 46. The effect of lime dose on organics (UVA removal from Mississippi River water.

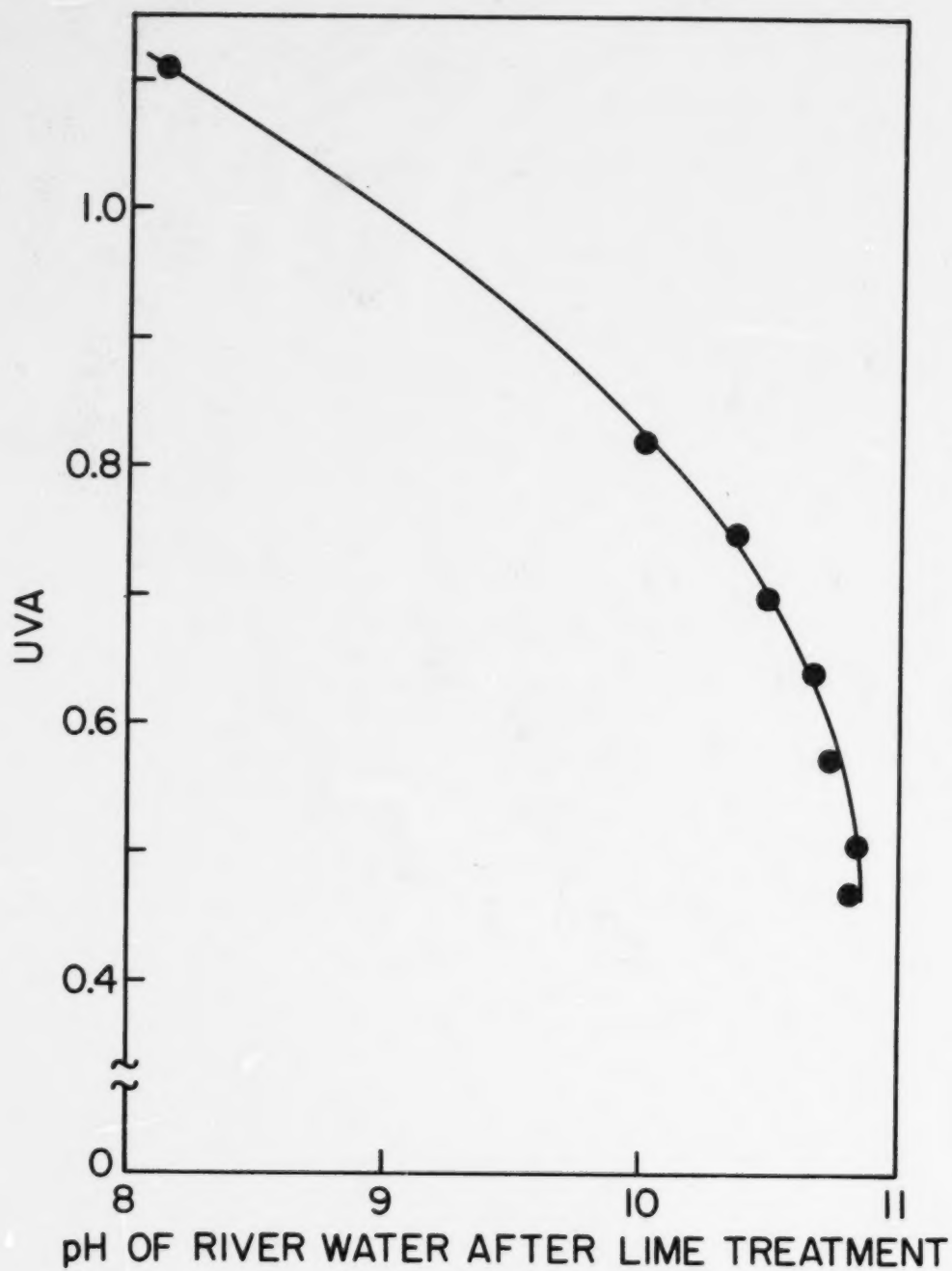


Figure 47. Organics (UVA) removal from Mississippi River water as a function of final pH following lime addition.

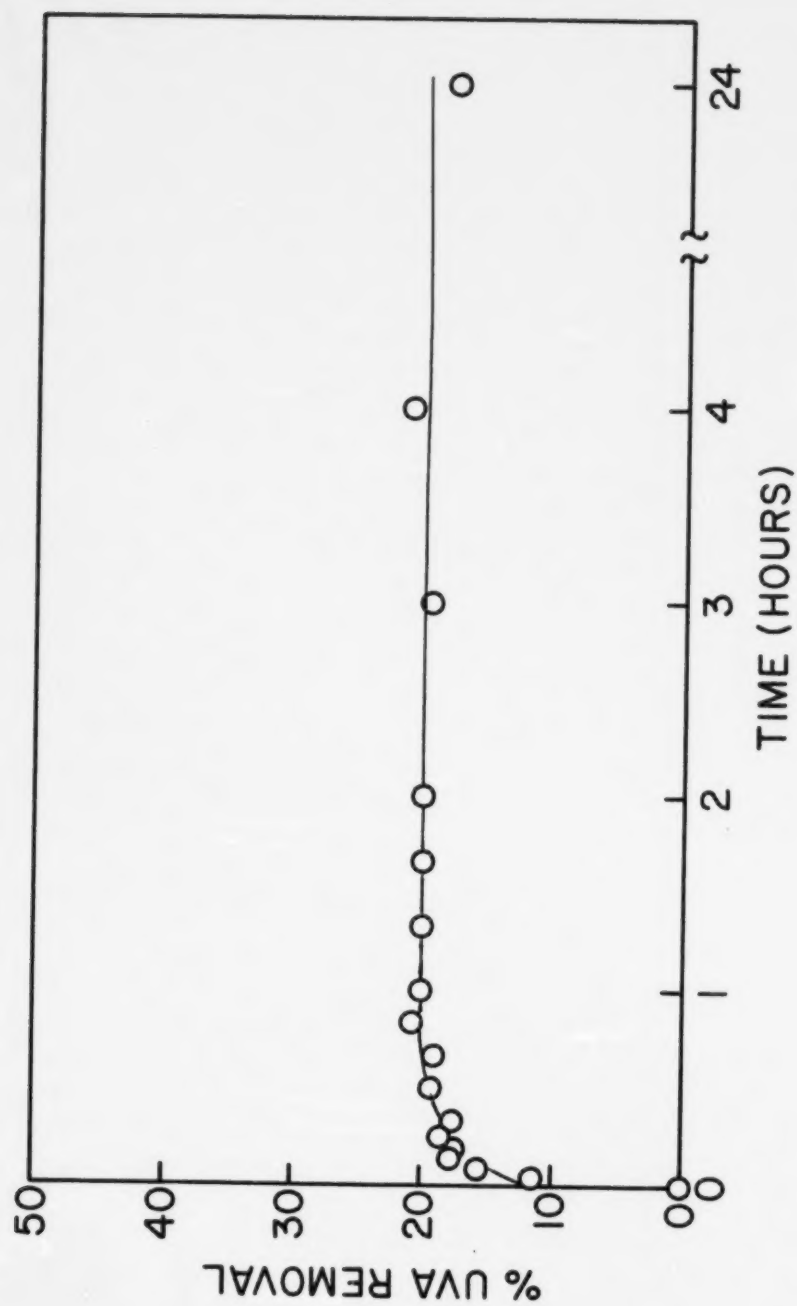


Figure 48. Kinetics of organics (UVA) removal from Mississippi River water treated with 230 mg/l as CaCO_3 time.

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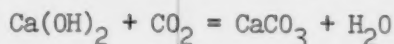
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that the kinetics of organics removal of the softening process were very rapid. Over 95% of the observed organics removal was complete within 30 minutes, the selected time for flocculation in the jar tests. It may be anticipated that for higher lime doses the greater amount of precipitate would cause the kinetics of organics removal to increase.

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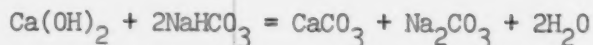
3. The Effect of Recarbonation on Organic Removal.

Having examined organics removal in the first stage of an excess lime treatment system, it was decided to investigate the influence of recarbonation. Carbon dioxide is most commonly used in the recarbonation step to neutralize excess lime according to following reaction:



and the additional precipitation of CaCO_3 may cause further removal of organics.

Two separate jar tests were conducted to investigate a number of variables pertinent to the recarbonation process. These variables included: the amount of excess lime employed during first-stage treatment, recarbonation dose, and speed of recarbonation rapid mix. The jar test procedure for these experiments on river water simulated actual water treatment practice in that it was performed in two stages. The first stage involved addition of the lime as a powder to a 500 mL sample, a 60-second rapid mix, flocculation for 30 minutes at 30 rpm and sedimentation for one hour. 250 mL of the supernatant were decanted off for the recarbonation stage. A sample of the remaining supernatant was filtered for analysis. Recarbonation was accomplished by adding sodium bicarbonate instead of carbon dioxide. The reaction may be written as follows:



Sodium bicarbonate was chosen for convenience and was added in powder form to the 250 mL sample of lime treated water. The sample was then either rapid or slow mixed depending on the sample. The sample was reflocculated at 10 rpm for 30 minutes on the gang stirrer before filtration and analysis.

Results from an experiment in which the lime dose was held constant in first-stage treatment and the bicarbonate dose varied in second-stage treatment and are shown in Figures 49 and 50. Figure 49 summarizes the hardness removal obtained in the two-stage process. As expected, additional calcium was removed by recarbonation while no significant change in magnesium levels was observed. The organics removal for each stage of treatment in this experiment are summarized in Figure 50. For all three organics parameters analyzed no significant trend was observed, and it was concluded that the additional calcium carbonate precipitate does not cause further removal of organics. Increasing the sodium bicarbonate dose from 80 to 120 mg/L as CaCO_3 had no effect on either hardness or organics removal as expected.

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Figures 51 and 52 summarize the results obtained when the excess lime

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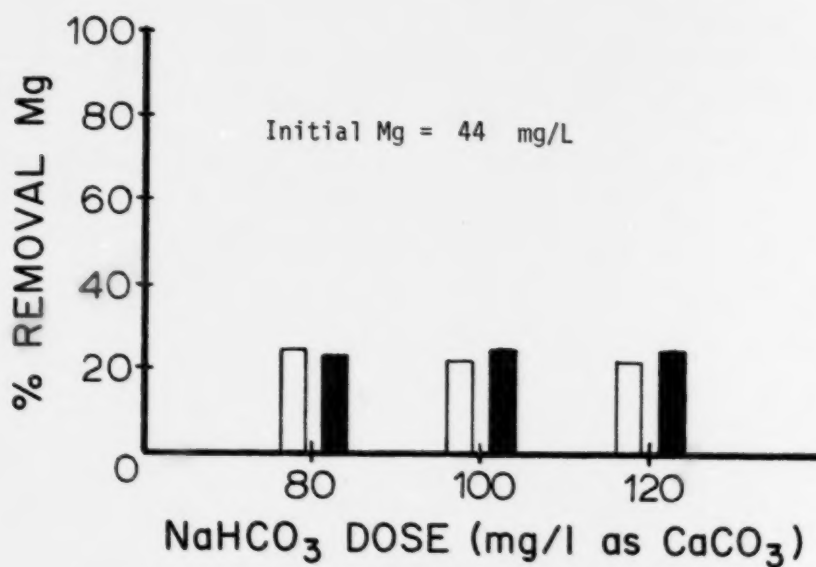
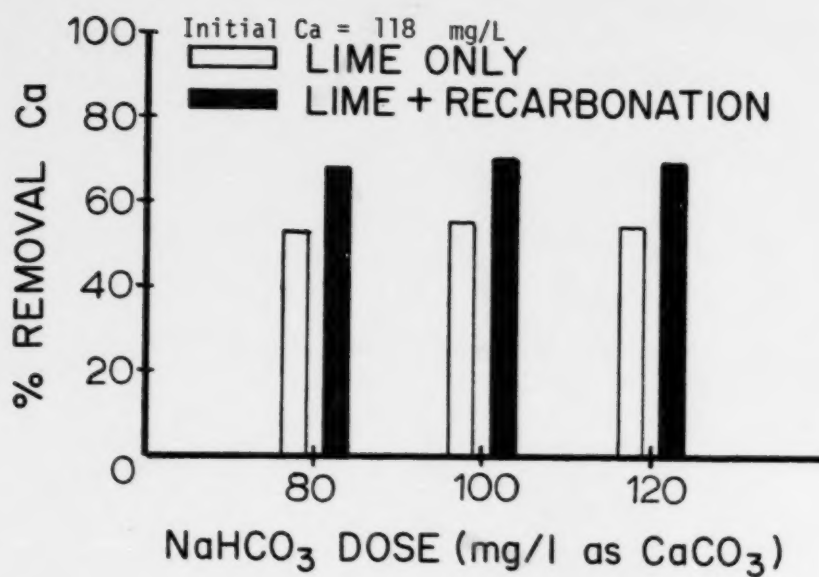


Figure 49. Effect on Mg and Ca removal of varying bicarbonate dose with lime dose constant at 200 mg/L as CaCO₃.

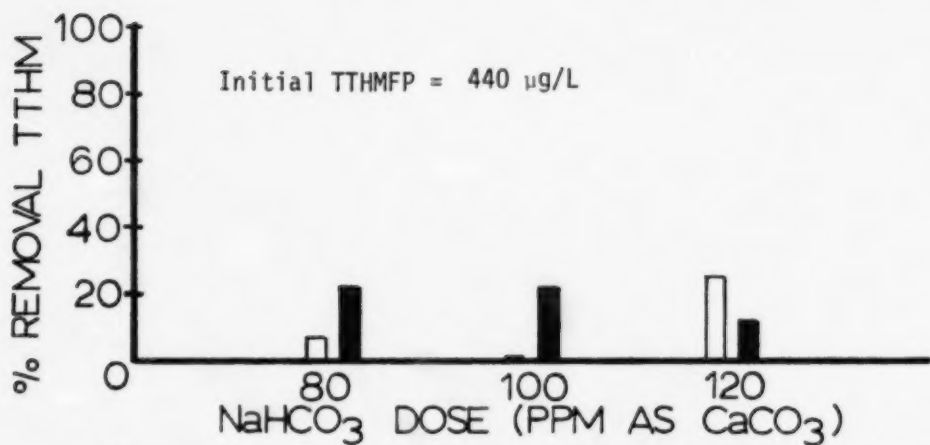
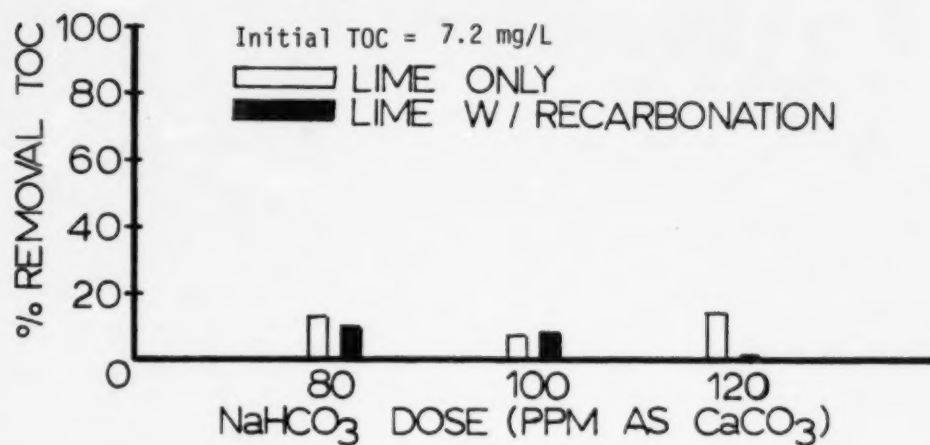
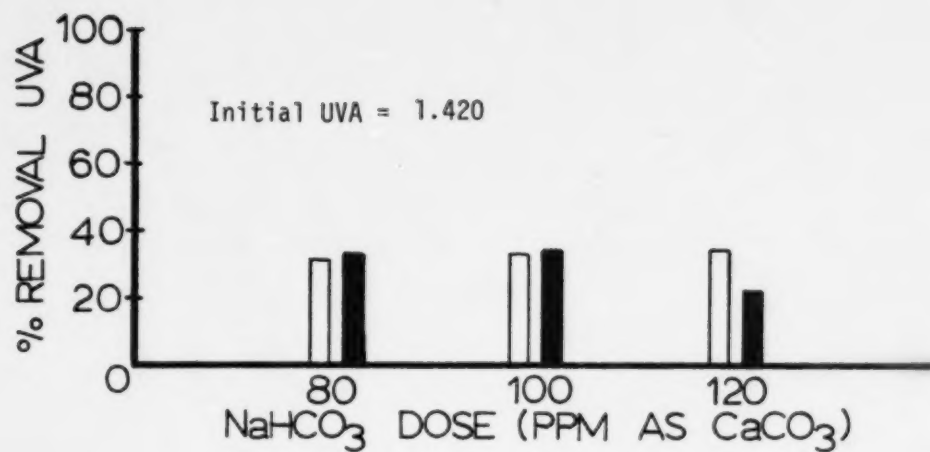


Figure 50. Effect on organics removal of varying bicarbonate dose with lime dose constant at 200 mg/L as CaCO₃.

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dose in the first-stage of treatment was varied. Sodium bicarbonate dosages were varied accordingly to reflect differences in the excess lime dose. In this study the amount of calcium carbonate precipitated during recarbonation should have increased with increasing excess lime dose and if the precipitation caused organics removal, a trend of increased removals should have been observed.

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Figure 51 shows the hardness removals obtained for this test. Calcium levels after the first-stage of treatment appeared to be the same for the four dosages examined. During recarbonation, however, a trend of increasing calcium removal with greater excess lime dose was observed. Magnesium removal during the first-stage of treatment can be seen to increase with higher excess lime dosages as one would expect due to increased pH. No significant trend for magnesium removal during recarbonation was apparent. The effect of varying the excess lime dose on organics removal during recarbonation is summarized in Figure 52. A moderate amount of variability in all three of the organics parameters measured makes interpretation of the data somewhat difficult, but it was concluded that varying the excess lime dose in the first-stage of treatment had no significant impact on organics removal during recarbonation.

The data shown in Figures 49-52 were obtained using a 60-second rapid mix for sodium bicarbonate addition. It was felt that perhaps too much energy was being put into the system causing poor coagulation and separation of particles. This may have accounted for some of the variability in the test results. A comparison was, therefore, made between sodium bicarbonate addition using a 60-second rapid mix and a slow mix accomplished by gentle swirling. The results from this experiment are summarized in Figure 53. Neither organics nor hardness removal appeared to be affected by the speed of mixing during chemical addition for recarbonation.

In summary, the small amount of fine, grainy, poor settling calcium carbonate precipitate formed during recarbonation was found to be ineffective in removing organics.

4. The Use of a Coagulant in Conjunction with Lime

The effect of coagulant dose, pH and order of additions will be discussed separately:

A. The Effect of Coagulant Dose

Discussions with personnel at the Minneapolis Water Treatment Plant revealed that they had found alum use in conjunction with lime to be beneficial in improving hardness removal and the settleability of solids in the softening process. A jar test was conducted to verify these observations and to evaluate the impact of coagulant use during lime softening on organics removal.

To separate the impact of the coagulant the lime dose was kept constant for all samples except for the river water control. Lime was added as a slurry by pipette at a dose corresponding to 50 mg/L as CaCO_3 excess lime.

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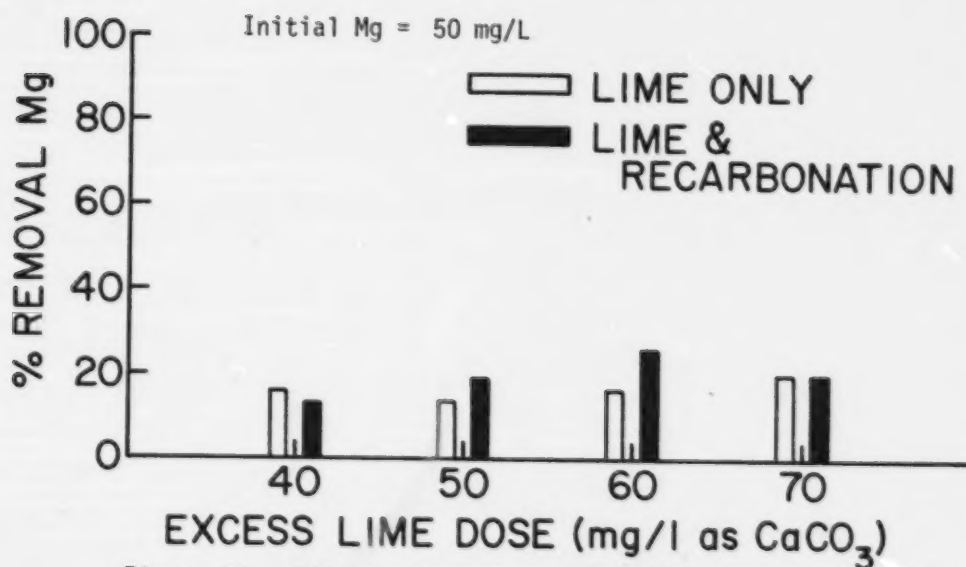
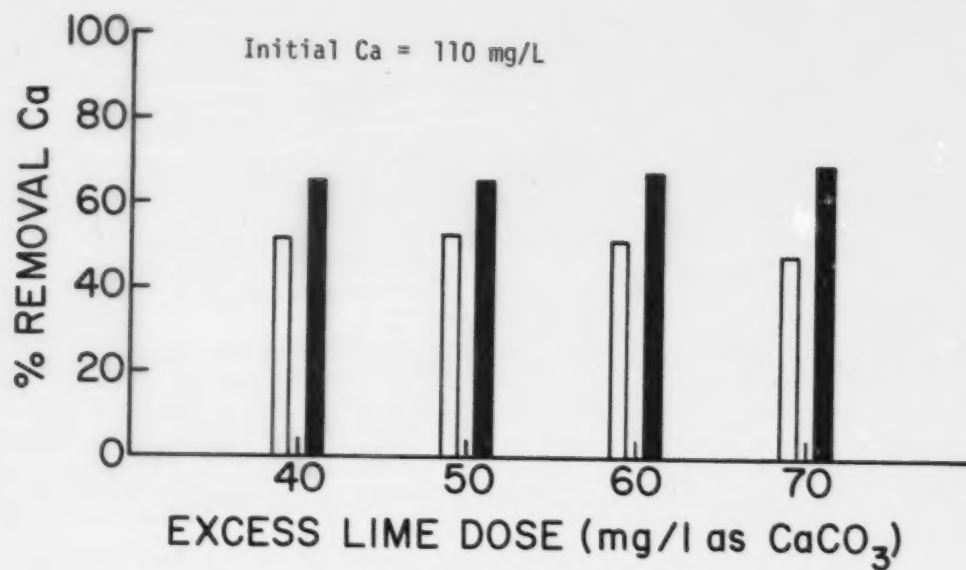


Figure 51. Effect of varying excess lime dose on residual Ca and Mg in treated Mississippi River water with and without recarbonation.

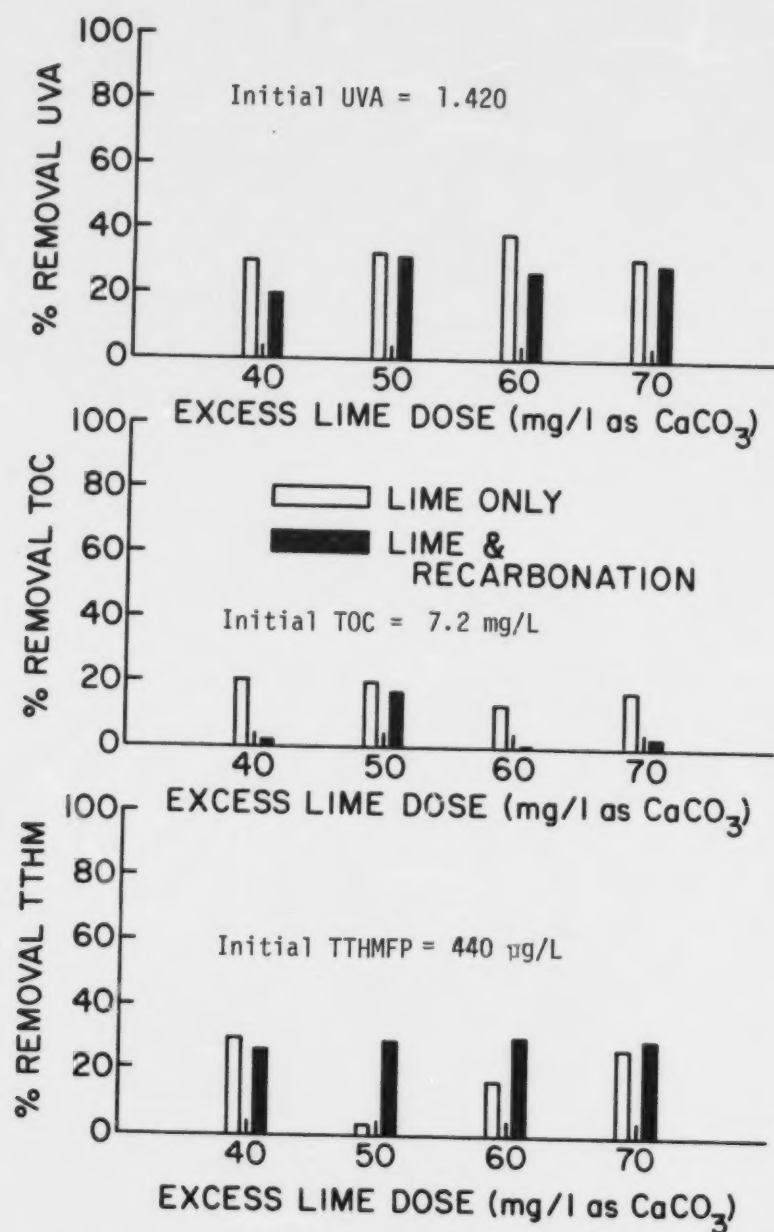


Figure 52. Effect of varying excess lime dose on organics removal from Mississippi River water with and without recarbonation.

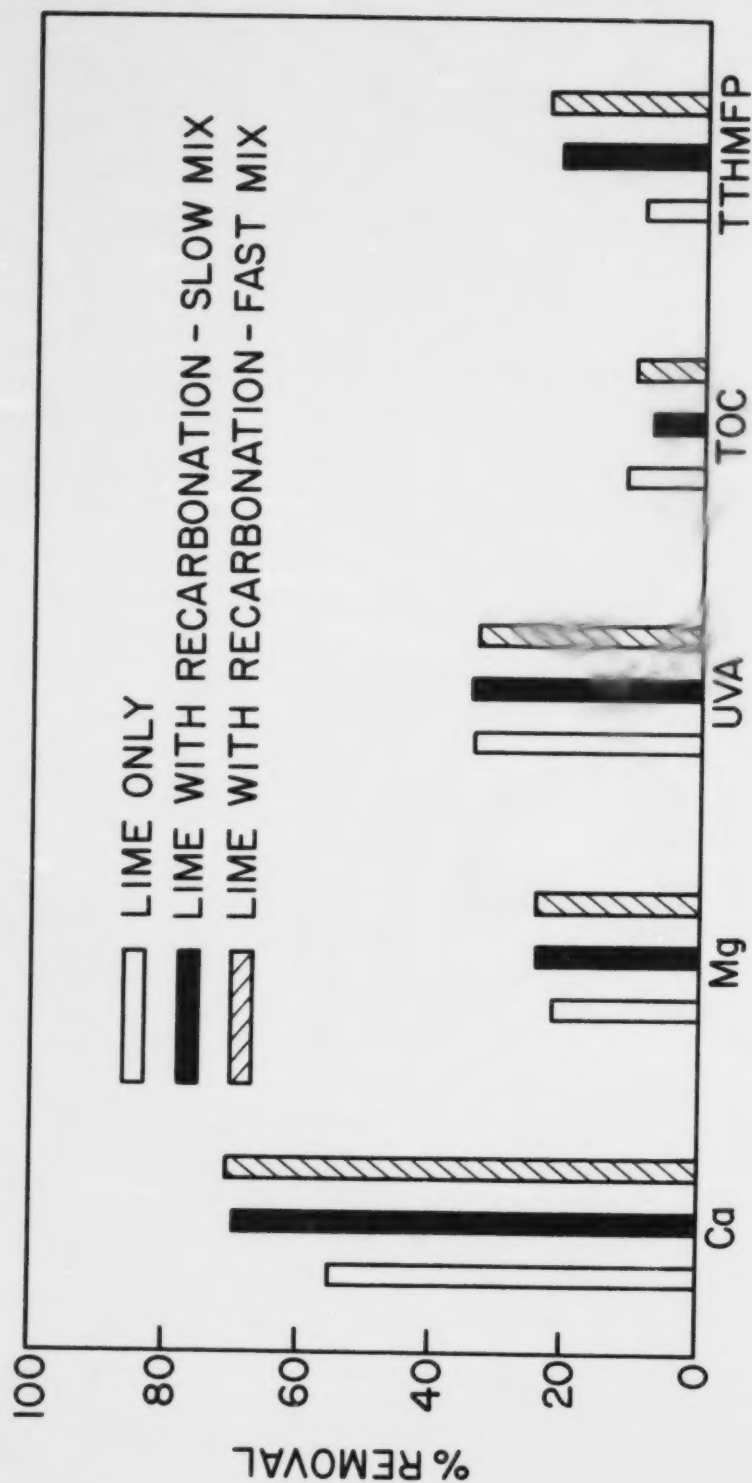


Figure 53. The effect of rapid mix speed during recarbonation on hardness and organics removal from Mississippi River water.

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Coagulants were added from 50 g/L stock solutions. The chemicals were added simultaneously to the vortex of a sample as it was rapid mixed. After lime and coagulant addition, the rapid mix was continued for 30 seconds. Flocculation for 30 minutes at 30 rpm was followed by settling for one hour and finally filtration through Whatman No. 1 filter paper. pH was measured after filtration.

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The hardness results from this test are illustrated in Figure 54. Lime treatment without recarbonation reduced the total hardness of the raw water from 182 to 102 mg/L as CaCO_3 , a reduction of about 44%. The optimum coagulant dose for total hardness removal was about 20 ppm for iron and 28-30 ppm for alum. Alum appeared to be more effective than iron, removing an additional 18% over lime treatment only.

Figure 55 summarizes the removal of organics as measured by UVA when coagulants were used in conjunction with lime during softening. The trends observed were very similar to those discussed above for total hardness removal. Lime treatment only reduced the UVA of the raw water by about 36%, but the addition of roughly 20 mg/L of coagulant improved removals to approximately 64%. Alum was marginally more effective than iron.

The addition of coagulant up to the optimum dose (15-25 mg/L) appeared to improve the coagulation/flocculation characteristics of the solution. However, with an increasing dose of the acidic coagulants the solution pH was reduced to the point that hardness removal was adversely affected. pH is shown in Figure 56.

The coagulant may improve removals by either acting directly, as a coagulant, on the organics or by improving the separation of precipitated solids. The latter process is considered more likely since the impact of the coagulant addition upon organics removal parallels the impact on hardness removal. Furthermore, many studies have observed that iron and alum are most effective for organics removal at much lower pH values (11). At the pH values experienced in excess lime softening direct removal of organics by the coagulant is considered unlikely (14).

B. The Effect of pH Control

In the above study on coagulant addition the true impact of a coagulant dose was clouded by the simultaneous effect of the coagulant on solution pH. To separate these effects another study was conducted in which the solution pH was controlled and maintained at the same level as the control (no added coagulant). Figure 57 compares the observed hardness removals in tests conducted with and without pH control. Calcium removals were essentially identical since in both cases the pH was sufficiently high to precipitate the same amount of CaCO_3 . However, the lower pH values that were developed in the uncontrolled study caused the removal of magnesium hydroxide to decline compared to the samples with a fixed pH.

A comparison of organics (UVA) removal during these studies provided the data shown in Figure 58. Unfortunately, the control samples did not

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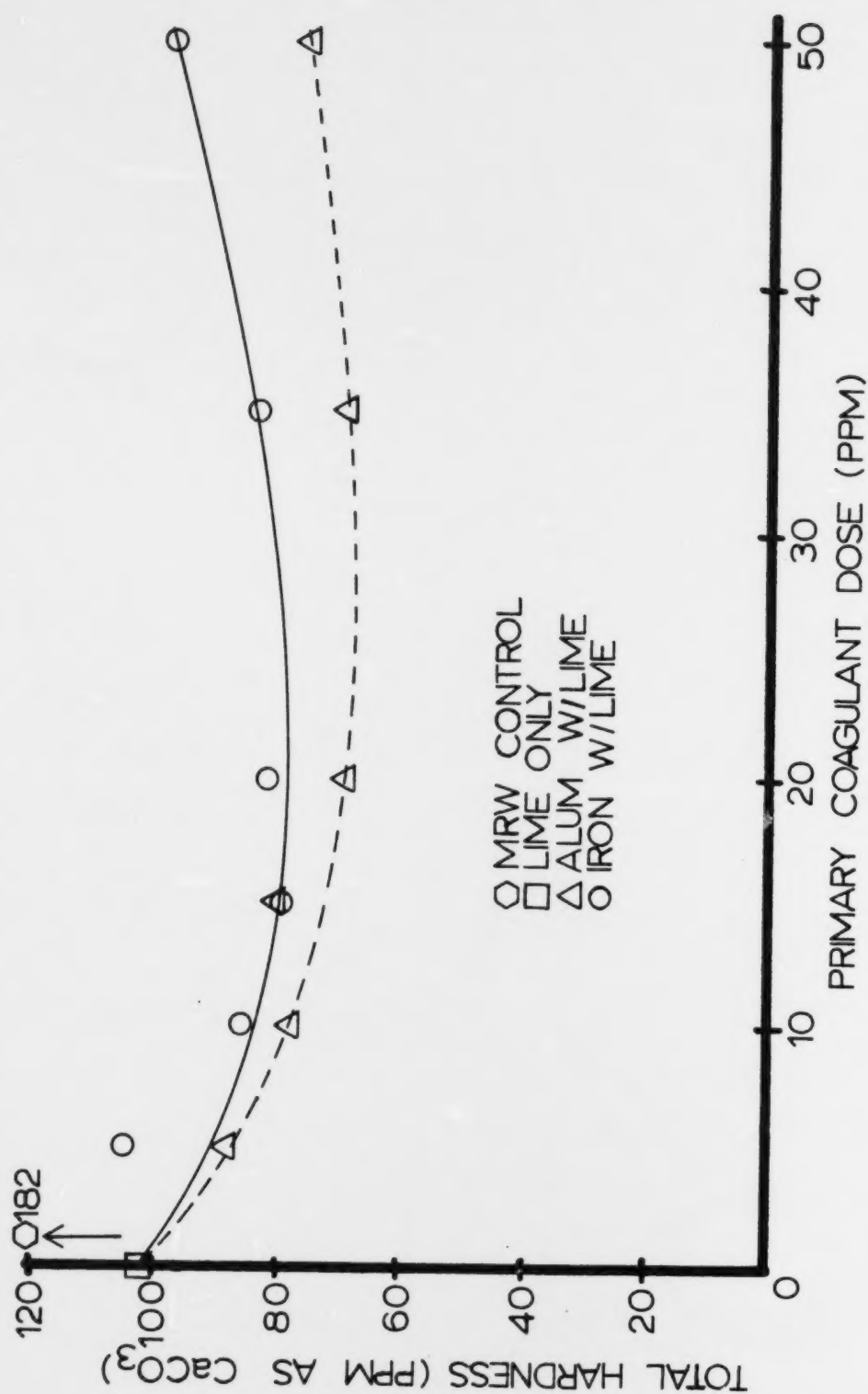


Figure 54. The use of a primary coagulant in conjunction with lime for removal of hardness from Mississippi River water lime dose $\approx$ 225 mg/l. The control (no lime, no coagulant) contained 182 mg/L hardness as CaCO_3 .

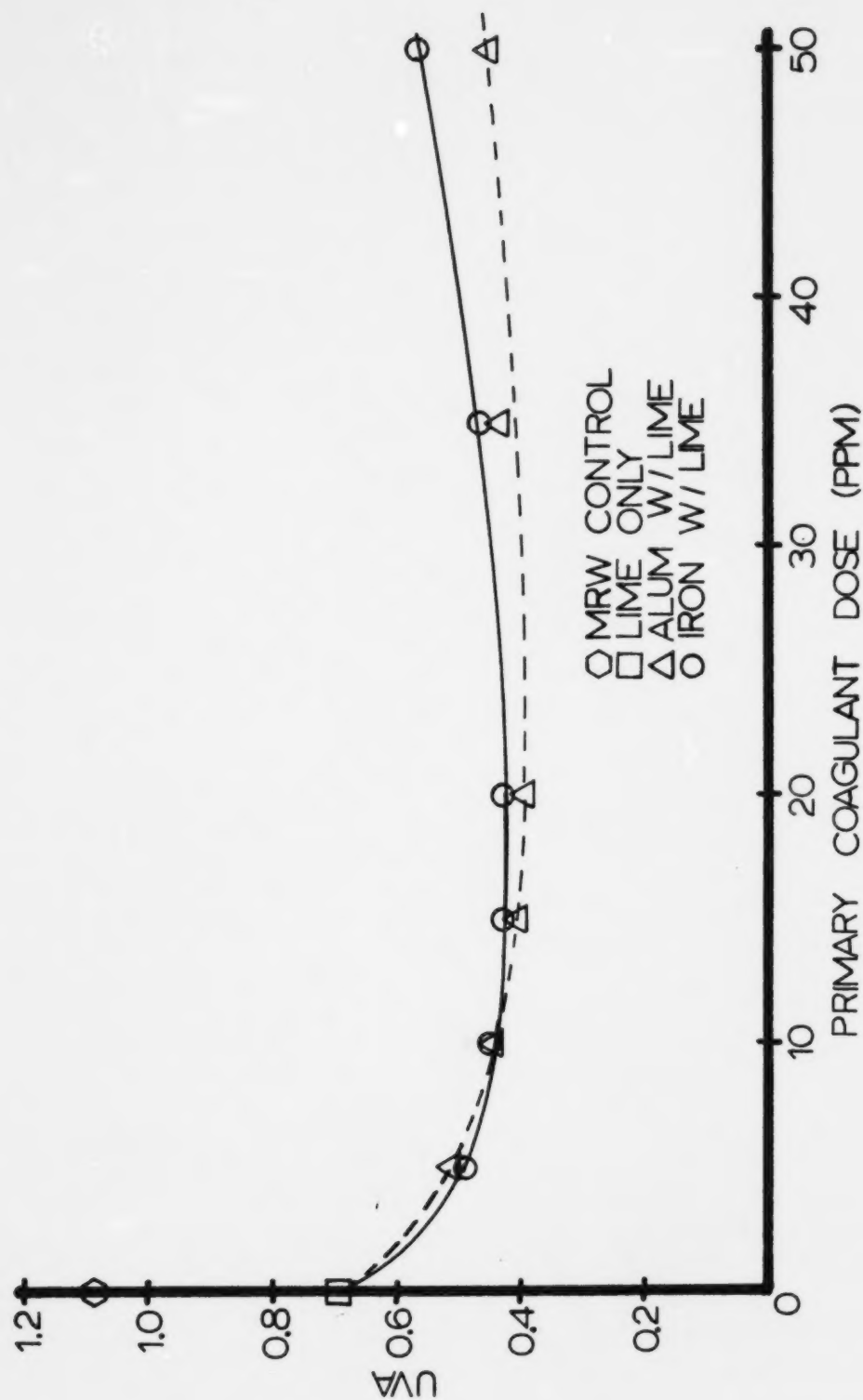


Figure 55. The use of a primary coagulant in conjunction with lime for removal of organics from Mississippi River water lime dose $\approx$ 225 mg/l.

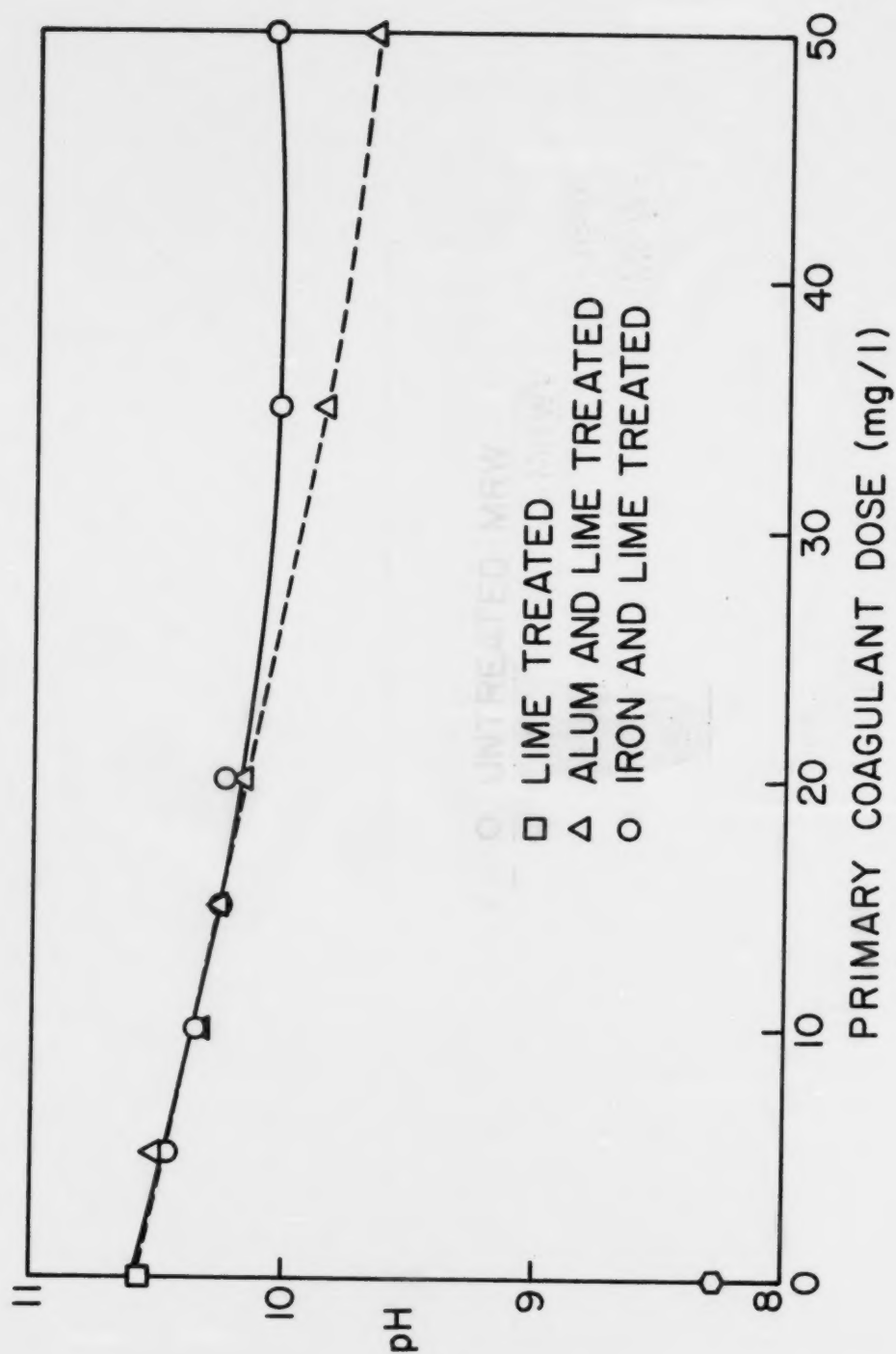


Figure 56. Influence of coagulant addition upon pH during the lime softening of Mississippi River water. Untreated water pH = 8.3.

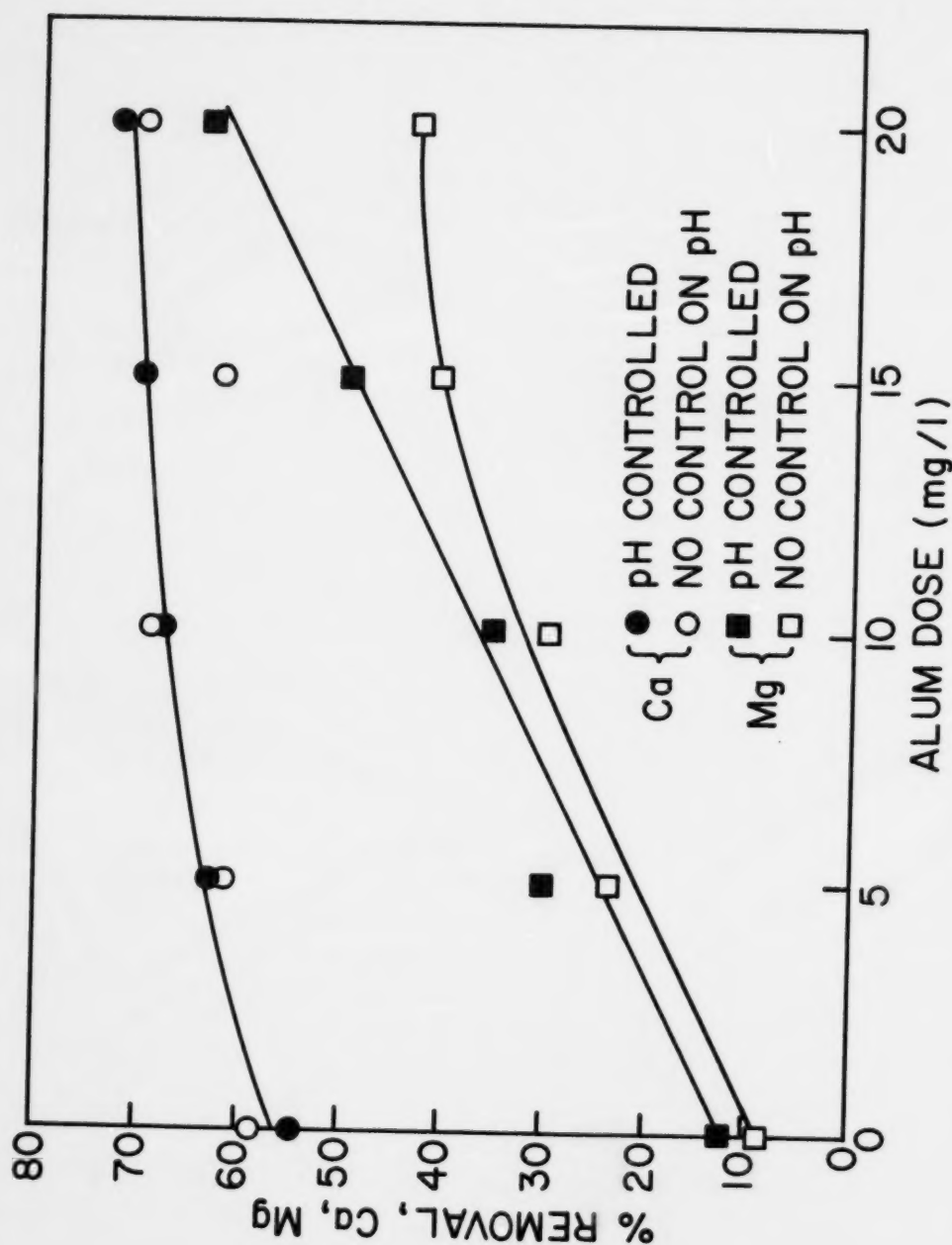


Figure 57. The effect of pH control on hardness removal from Mississippi River water by lime and alum.
 Lime dose $\approx$ 225 mg/L as CaCO_3 , Initial Ca $\approx$ 128 mg/L as CaCO_3 , Initial Mg $\approx$ 54 mg/L as CaCO_3

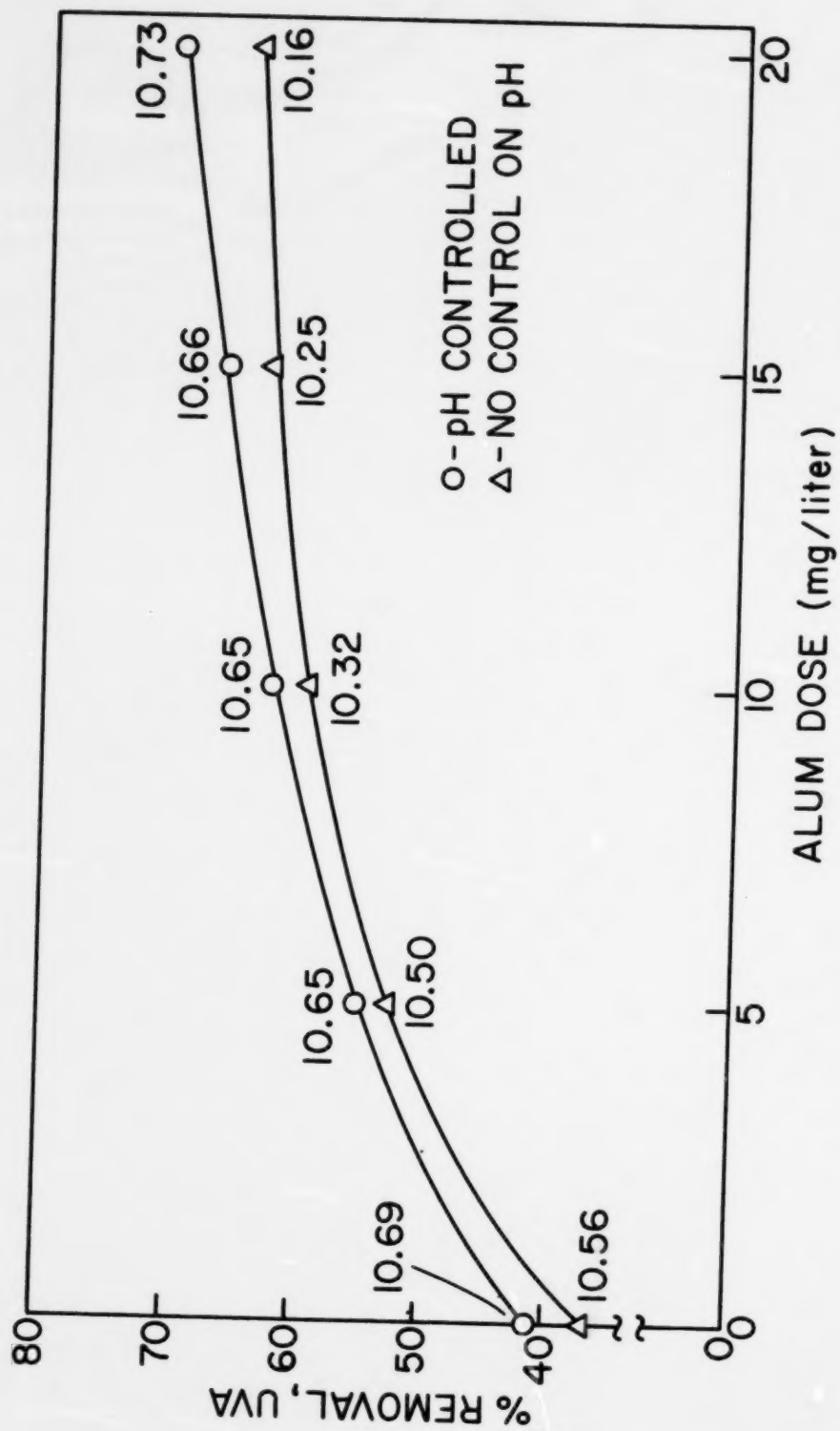


Figure 58. Effect of pH control on organics removal from Mississippi River water by alum and time. (Same conditions as Figure 57).

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yield the same levels of organics removal. The difference in the performance of the controls appeared to stem in part from the different final pH values that were attained in the studies. In the pH controlled study the pH reaches 10.69 whereas in the uncontrolled study it only reached 10.56. This small discrepancy may account for the 4% difference in performance observed. To correct for this effect the initial regions of the curve were superimposed as shown in Figure 59.

Because it was necessary to apply a correction before comparing the controlled and uncontrolled pH sample sets, conclusions drawn from this data can not be made with the confidence one would desire. However, in comparing Figures 57 and 59 it may be argued that for the samples with no pH control the point where the magnesium removal curve begins to level off is also the point on the UVA removal curve where little further removal is observed for the sample set that was controlled. The removal of magnesium was a linear function of alum dose (Figure 57). It is interesting to note in Figure 58 that UVA is also a linear function of alum dose in the range from 10 to 20 mg/L. These observations tend to support the theory that the alum is acting to remove precipitates of CaCO_3 and $\text{Mg}(\text{OH})_2$ that have organics absorbed or entrained with them.

C. Effect of Order of Addition

A brief experiment was conducted to evaluate the order of addition of lime and alum. A lime dose of 226 mg/L as CaCO_3 and an alum dose of 15 mg/L were chosen. When the two chemicals were added at the same time, a 30-second rapid mix was used before the sample was placed on the gang-stirrer. When the two chemicals were not added at the same time, the following procedure was used:

- 1) add chemical No. 1 to the rapid mix
- 2) rapid mix for 30 seconds
- 3) slow mix for one minute
- 4) add chemical No. 2 to sample at slow mix speed
- 5) place sample on gang-stirrer

The one-minute slow mix time was somewhat arbitrarily chosen to reflect the time of mixing that would occur in practice if one of the chemicals were fed to the influent line to a solids contact reactor before it actually reached the main rapid mix unit. The results from this study are shown in Figure 60. They indicate that the order of addition of lime and alum had essentially no effect on either organics or hardness removal.

5. The Effect of Sodium Aluminate Use in Conjunction with Lime

Sodium aluminate offers many benefits over alum when used for lime softening. Although more expensive than alum, research by the Nalco Chemical Company (58) indicates that sodium aluminate is much more effective as a coagulant since it is alkaline rather than acidic in character. Its use during softening results in lower lime and soda ash dosages. For these reasons a jar test was conducted to evaluate the performance of sodium alumin-

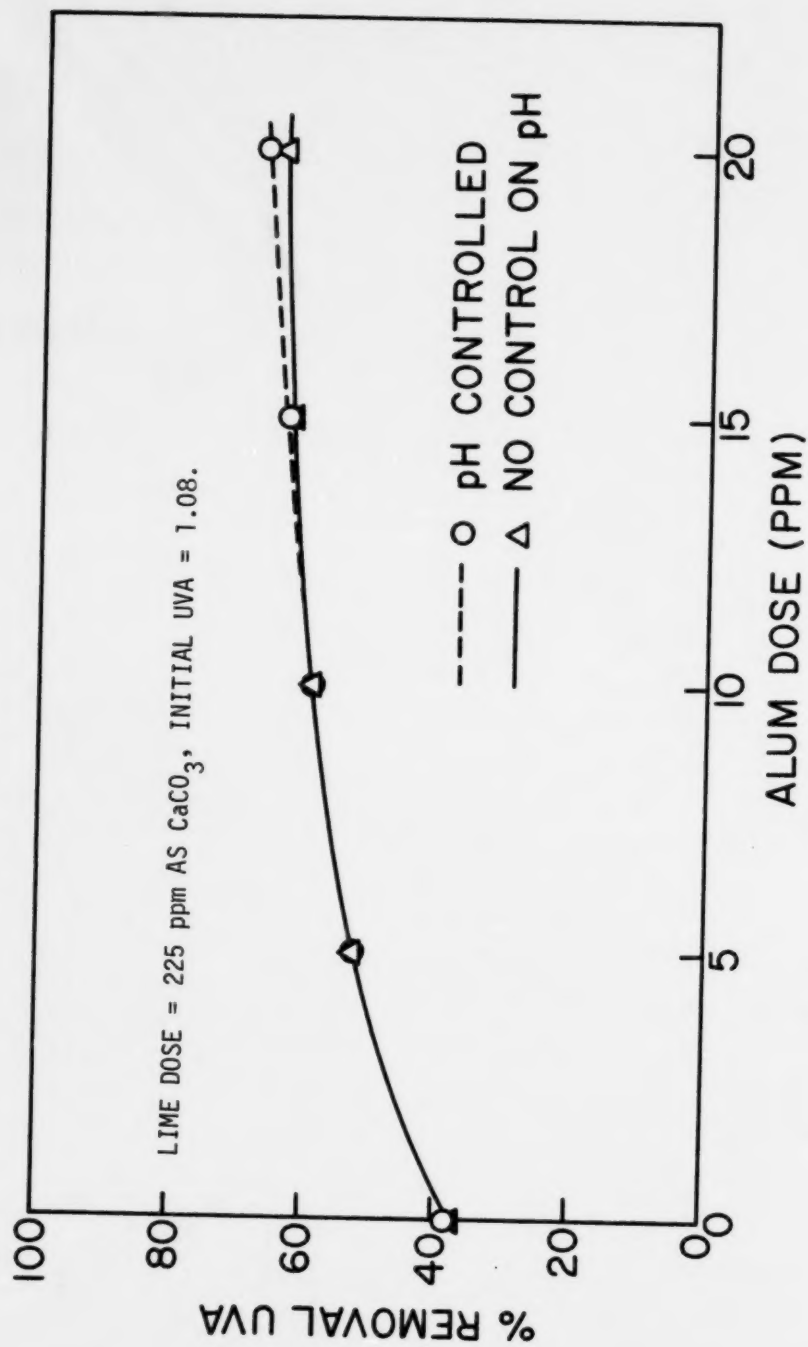


Figure 59. The effect of pH control on organics removal from Mississippi River water by alum and lime.

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ate with lime for organics removal.

The experimental procedure for this test was the same as that used for the studies with alum. Sodium aluminate solution was added at the same time as the lime. For comparison alum dosages of 10 and 20 ppm were also run in conjunction with lime. No pH control was employed on any of the samples.

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Hardness removal results for this test are presented in Figure 61. Sodium aluminate dosages were converted to equivalent alum dosages to facilitate direct comparisons between the two coagulants. As can be seen from the figure, there appears to be no significant difference between the performance of sodium aluminate and alum in the dosage range from 0 to 20 ppm. It should be noted, however, that at dosages greater than 20 ppm hardness removal continued to improve for sodium aluminate whereas previous experiments indicated that alum doses greater than 20 ppm were detrimental to both hardness and organics removal.

Figure 62 summarizes the organics removal as measured by UVA for sodium aluminate use with lime. As for hardness removal, sodium aluminate performed identically to equivalent alum dosages. Continued improvement in UVA removal, although slight was observed for sodium aluminate dosages greater than 20 ppm.

The relative performance of the two coagulants tested were expected to be very similar. In solution at the elevated pH values present in softening both coagulants will dissolve to produce aluminate, $\text{Al}(\text{OH})_4^-$ ions. The only difference between the coagulants is their effect on solution pH. Each molecule of alum requires 8 OH^- ions to form two aluminate ions and this requirement causes the pH of solution to drop. Sodium aluminate, however, is alkaline in nature and has little impact on pH when added during softening.

6. The Effect of Polymer Use with Alum and Lime

Various combinations of cationic polymer (Arco 6320-P) and alum dosages were evaluated in a standard jar test for their impact on organic removal during softening. All chemicals were added simultaneously to the rapid mix. Lime was added as a slurry at a concentration of 226 ppm as CaCO_3 which corresponds to 50 ppm as CaCO_3 excess lime. Cationic polymer was prepared according to the manufacturer's specifications and delivered by volumetric pipette. All permutations of 0, 1, 3 and 5 ppm polymer and 0, 7, 14 and 20 ppm alum were examined.

The results of polymer use on total hardness and organics removal are depicted in Figures 63 and 64, respectively. Polymer use actually appeared to be slightly detrimental to hardness removal. This trend was observed for all alum doses studied.

Figure 64 also shows that increasing the polymer concentration for any given alum dose seemed to decrease organics removal.

The number of different types of polymers currently being produced is vast. Testing one cationic polymer on one certain water does not allow gen-

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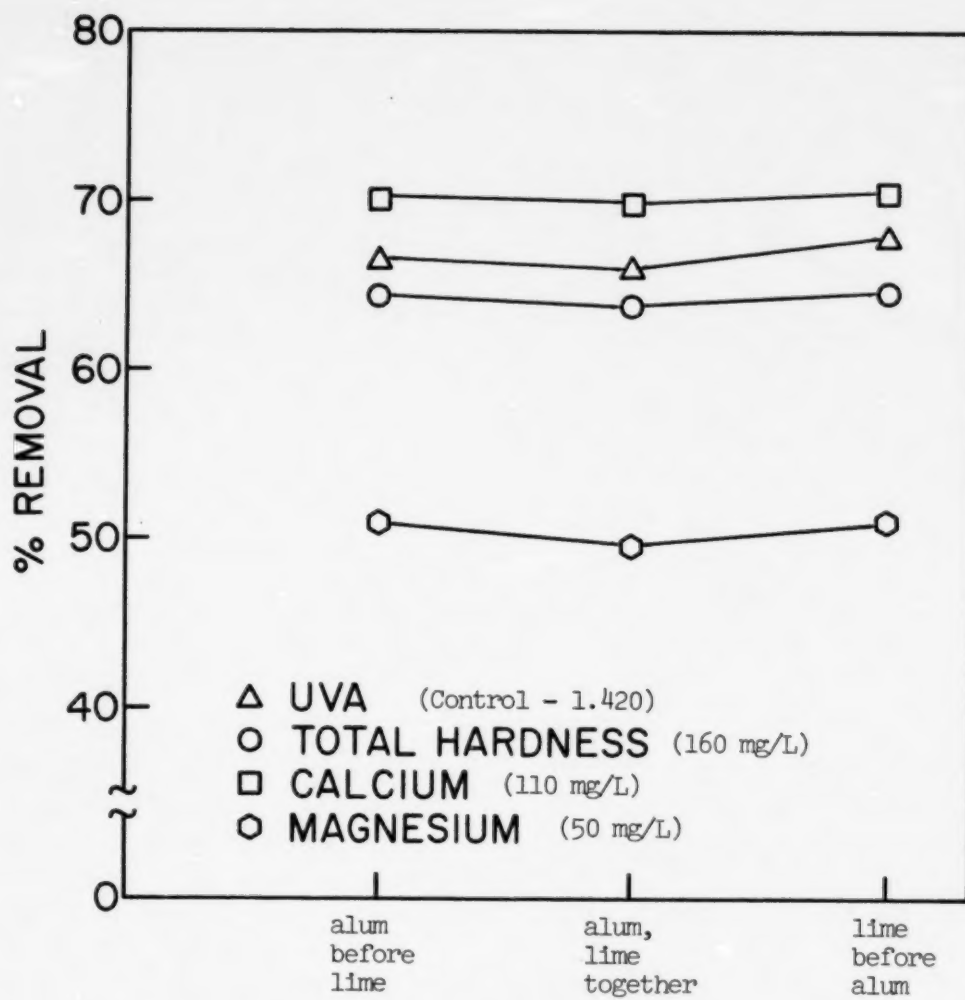


Figure 60. The influence of order of addition: lime and alum treatment of river water.

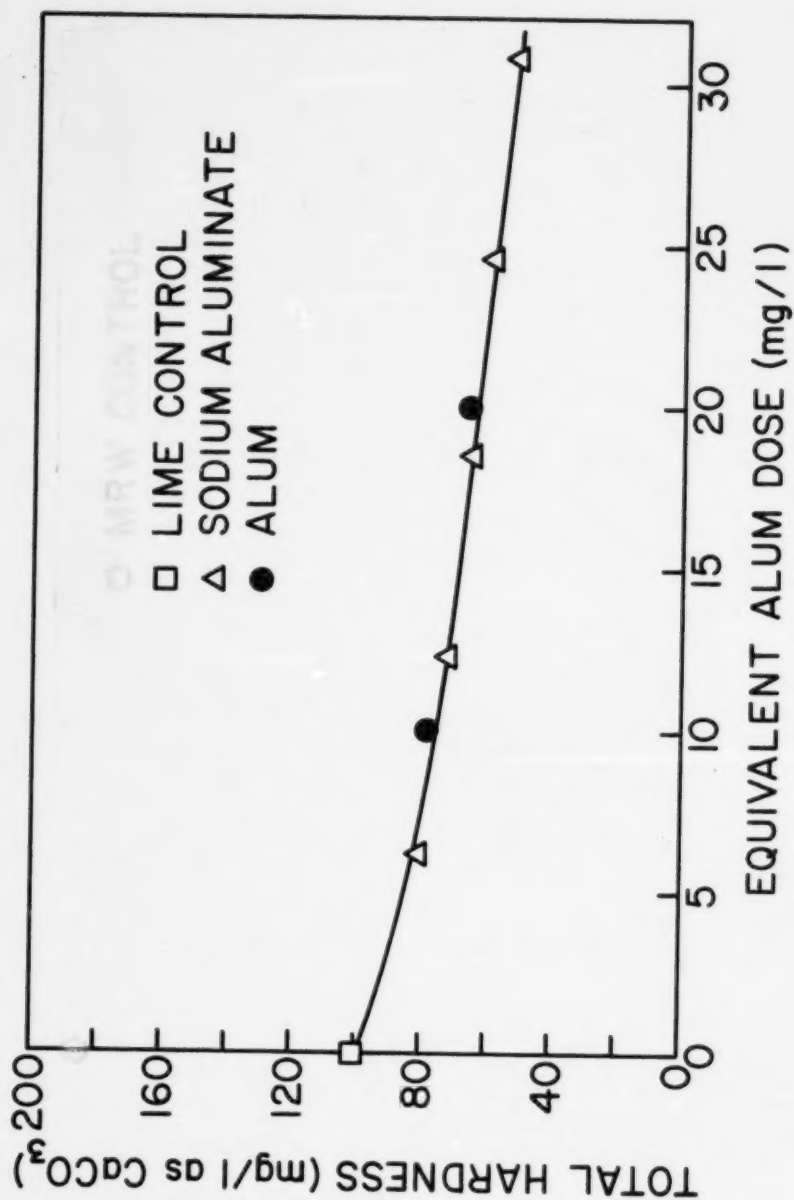


Figure 61. The effect of sodium aluminate (NaAlO_2) use in conjunction with lime on hardness removal from Mississippi River water. Initial hardness - 182 mg/L as CaCO_3 .

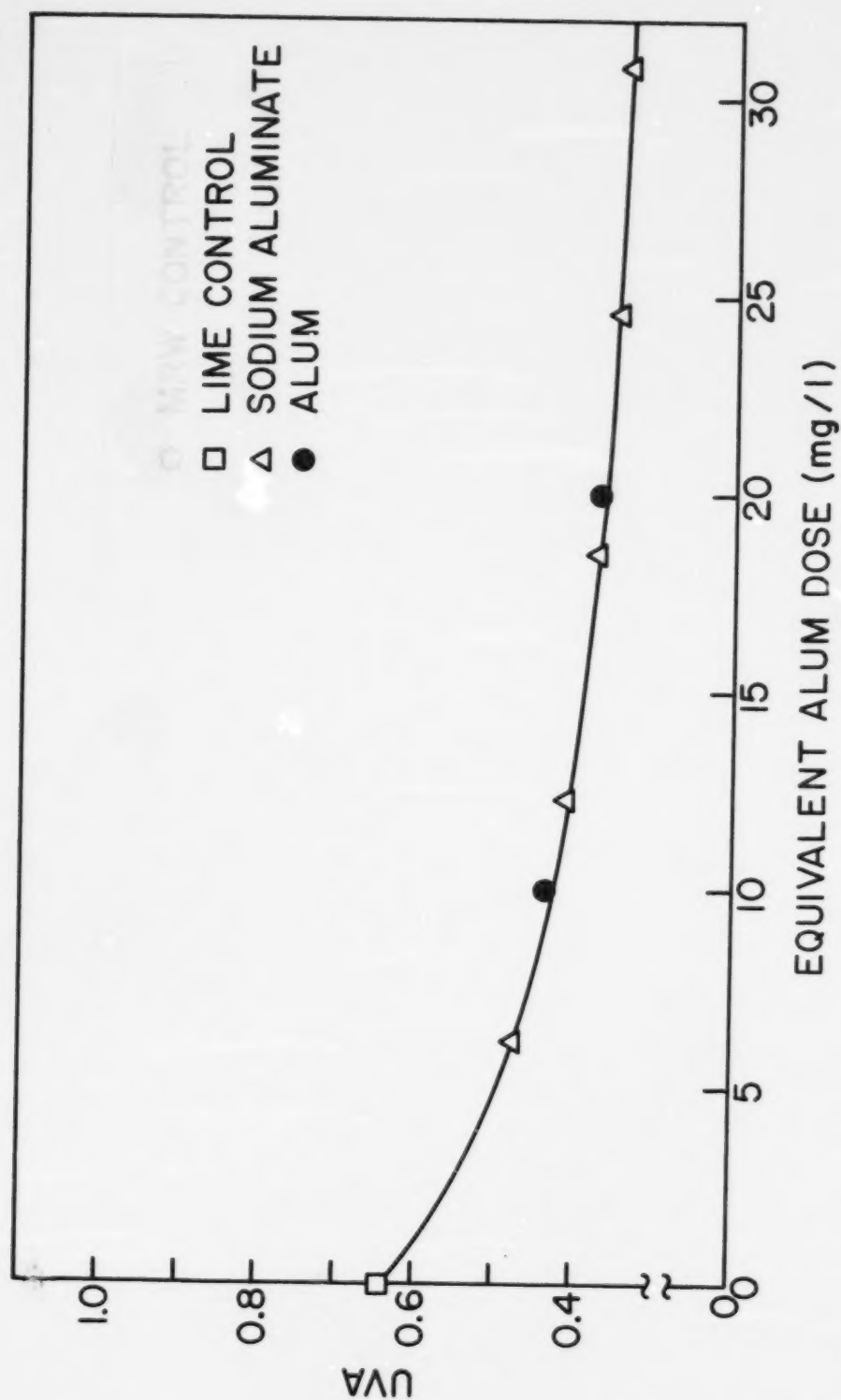


Figure 62. The effect of sodium aluminat (NaAlO_2) use in conjunction with lime on organics removal from Mississippi River water. Initial UVA - 1.08.

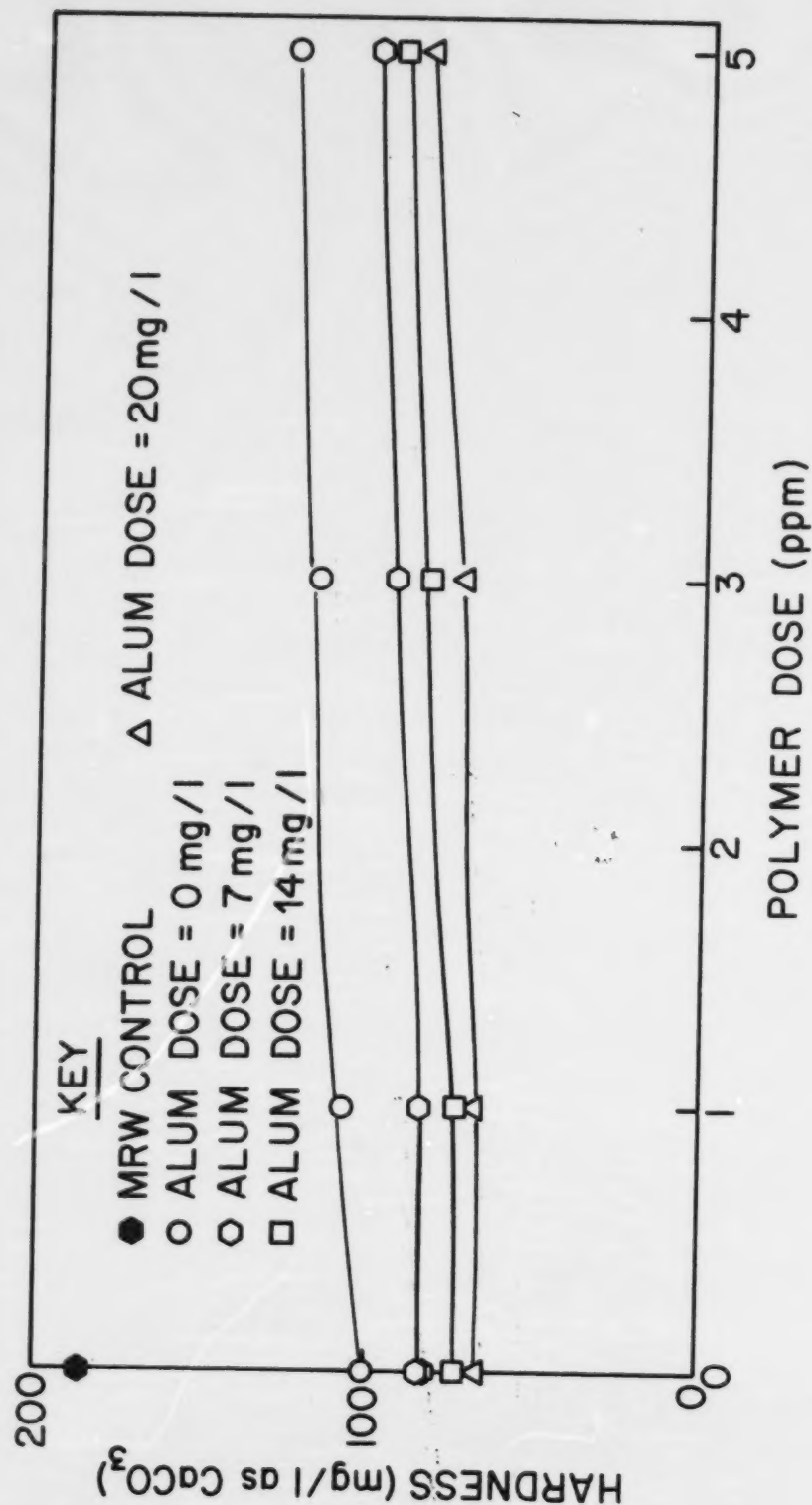


Figure 63. The influence of polymer (ARCO 6320-P) on hardness removal with and without alum addition during lime softening of Mississippi River water. Initial hardness = 182 mg/L as CaCO_3 .

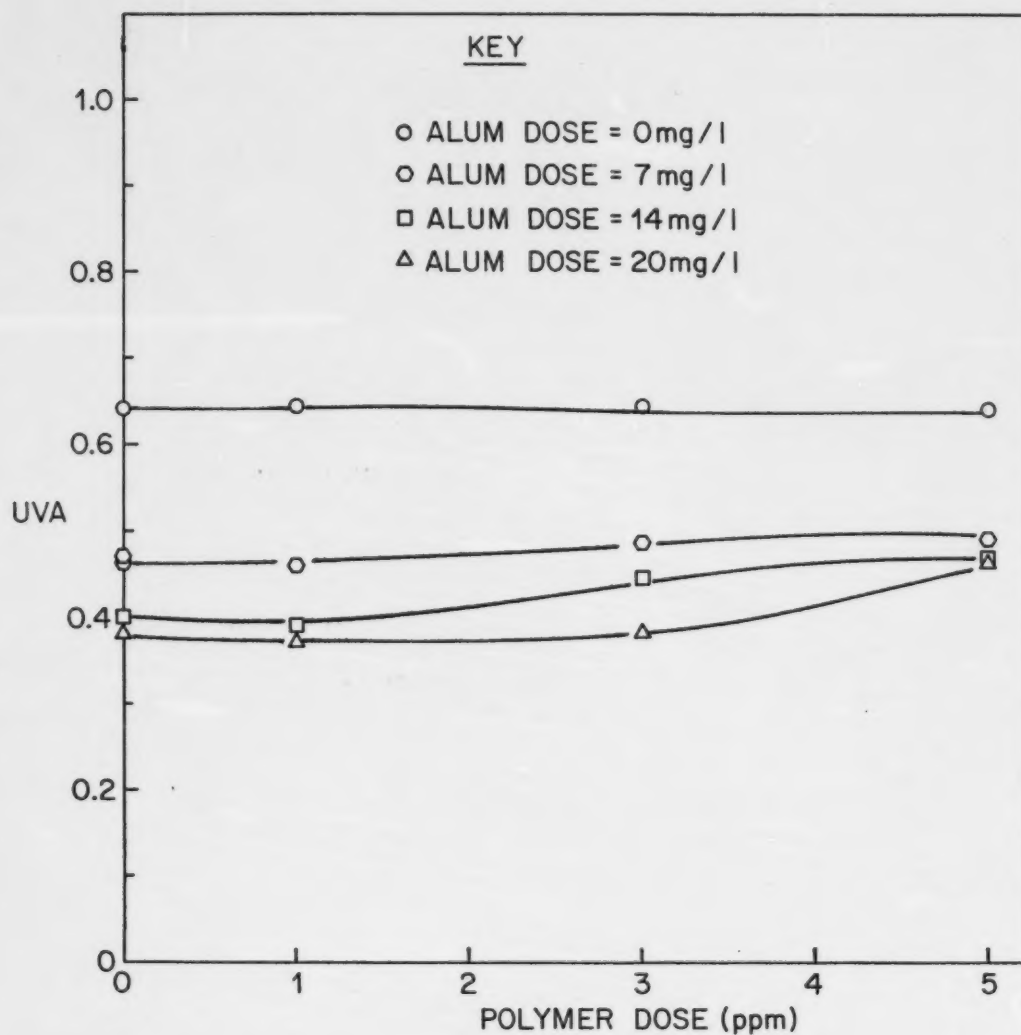


Figure 64. The influence of polymer (ARCO 6320 P) on organics removal with and without alum addition during the lime softening of Mississippi River water. Initial UVA = 1.08.

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eralization on its use. Polymers may have an application in the lime softening process depending on specific conditions encountered. However, in this study the cationic polymer tested showed no benefit.

7. Varying Magnesium Levels in the Raw River Water

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An experiment was conducted to evaluate the impact of precipitating varying amounts of $Mg(OH)_2$ on organics removal. The magnesium concentration was varied by spiking the raw river water with solutions containing different concentrations of $MgSO_4$. pH control was accomplished by the addition of 1N NaOH (i.e., no lime was used). Figure 65 illustrates the results from this study for organics removal at three different pH values. A more valuable plot is shown in Figure 66 which presents the organics removal as a function of the amount of magnesium removed in the softening process. This figure indicates that the solution pH maintained during the softening process was more important than the amount of magnesium hydroxide precipitated. As shown in Figure 66, for the same amount of $Mg(OH)_2$ precipitation (e.g., 10 mg/L as $CaCO_3$) increasing the pH from 10.25 to 10.9 caused the % organics removal to increase from 10 to 25%. The precipitates formed at pH 10.6 and 10.9 were much more flocculant than the precipitate formed at pH 10.2. But apart from this observation no other differences were noted between the tests conducted at the different pH values.

The final hardness of the water samples was not identical. The residual hardness was observed to increase with increasing initial magnesium concentration as shown in Figure 67. This probably reflects a kinetic effect because the final hardness should be determined by the treatment pH and it should be independent of the initial hardness for a given treatment pH.

As discussed above in Section 3, the correlation between TOC and UVA was always found to be good and in both lime and alum treated waters correlations were obtained that indicated that TOC and TTHMFP removals could be estimated by UVA measurements. This is not to imply that the % removals of TOC and TTHMFP are equal to UVA removals. TOC and TTHMF were never removed to the same extent as UVA in any of the pretreatment studies. Therefore, the significant increase in UVA removal at elevated pH in the softening process is a real indication of improved organics removal. Since the pH was always adjusted to pH 4.0 prior to UVA analyses, the influence of pH on the absorbance of organic compounds was eliminated.

Since studies were conducted with exactly the same amounts of $Mg(OH)_2$ removal at different pH values, it is not possible to argue that the poorer performance at lower pH was purely a solids separation problem. Instead, the improved removal of organics at higher pH values must be explained by improved absorption to the precipitated solids at elevated pH values.

As pH is increased, the surface of the magnesium hydroxide becomes more negatively charged. In addition, the negative charge on the humic and fulvic acid content of the water remains unchanged or increases slightly. The increase may be caused by the dissociation of phenolic groups. However, in the pH range of 10.2 to 10.9 the pH of most phenolic groups is likely exceeded sufficiently such that any increase in negative charge would be slight. It

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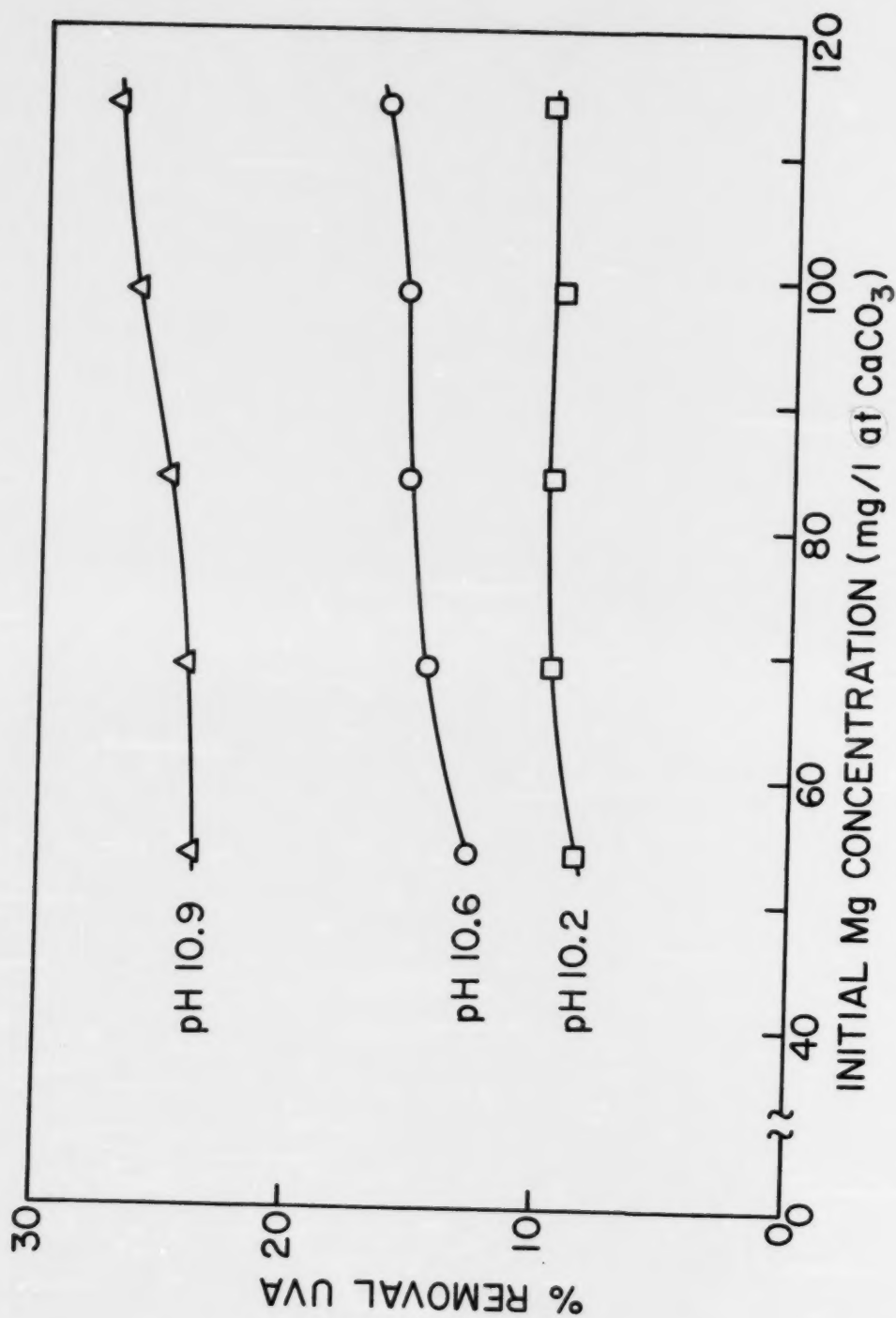


Figure 65. Effect of varying initial magnesium concentration on organics removal from Mississippi River water. Initial UVA = 1.08.

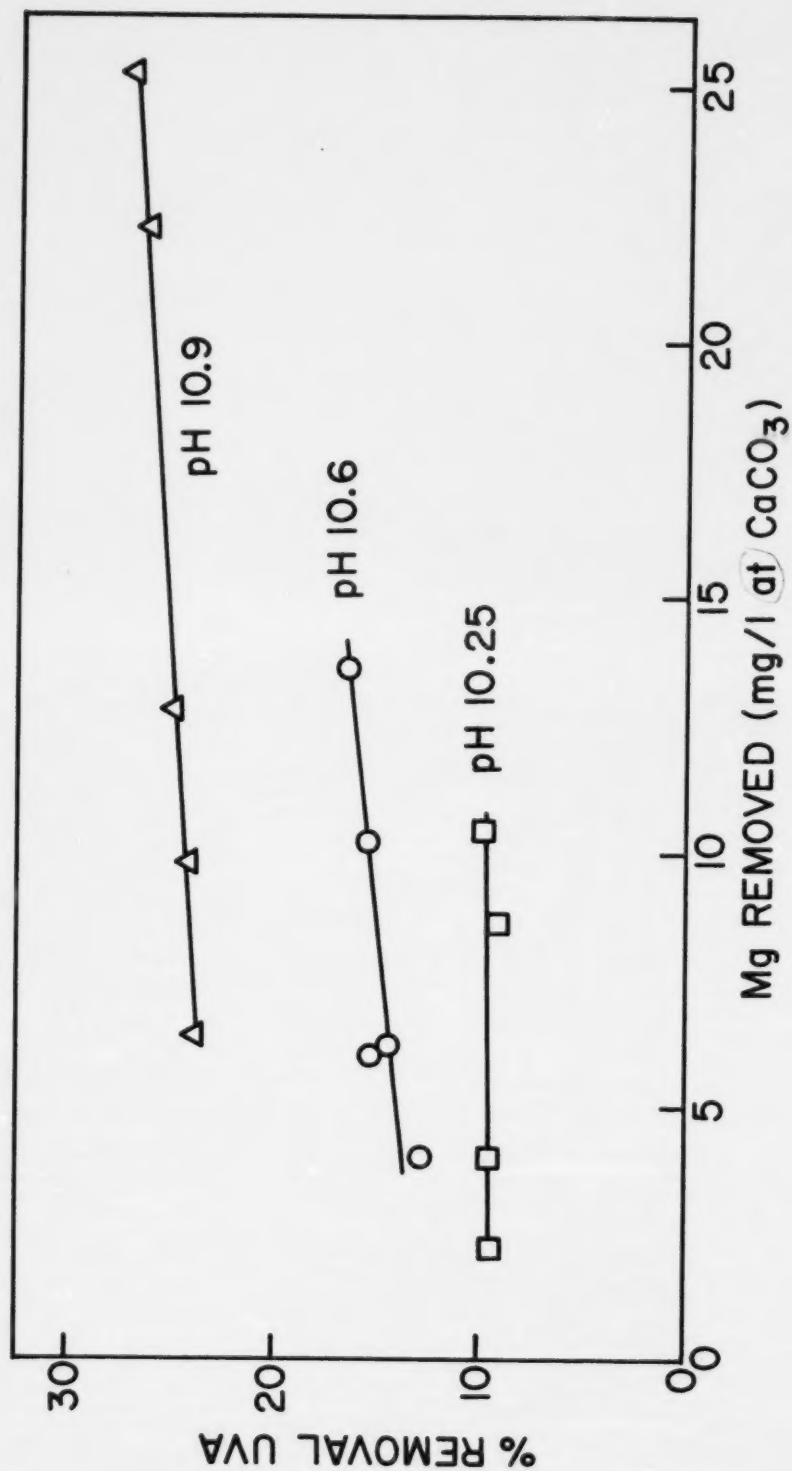


Figure 66. Effect of $\text{Mg}(\text{OH})_2$ precipitation on organics removal from Mississippi River water. Initial UVA = 1.08.

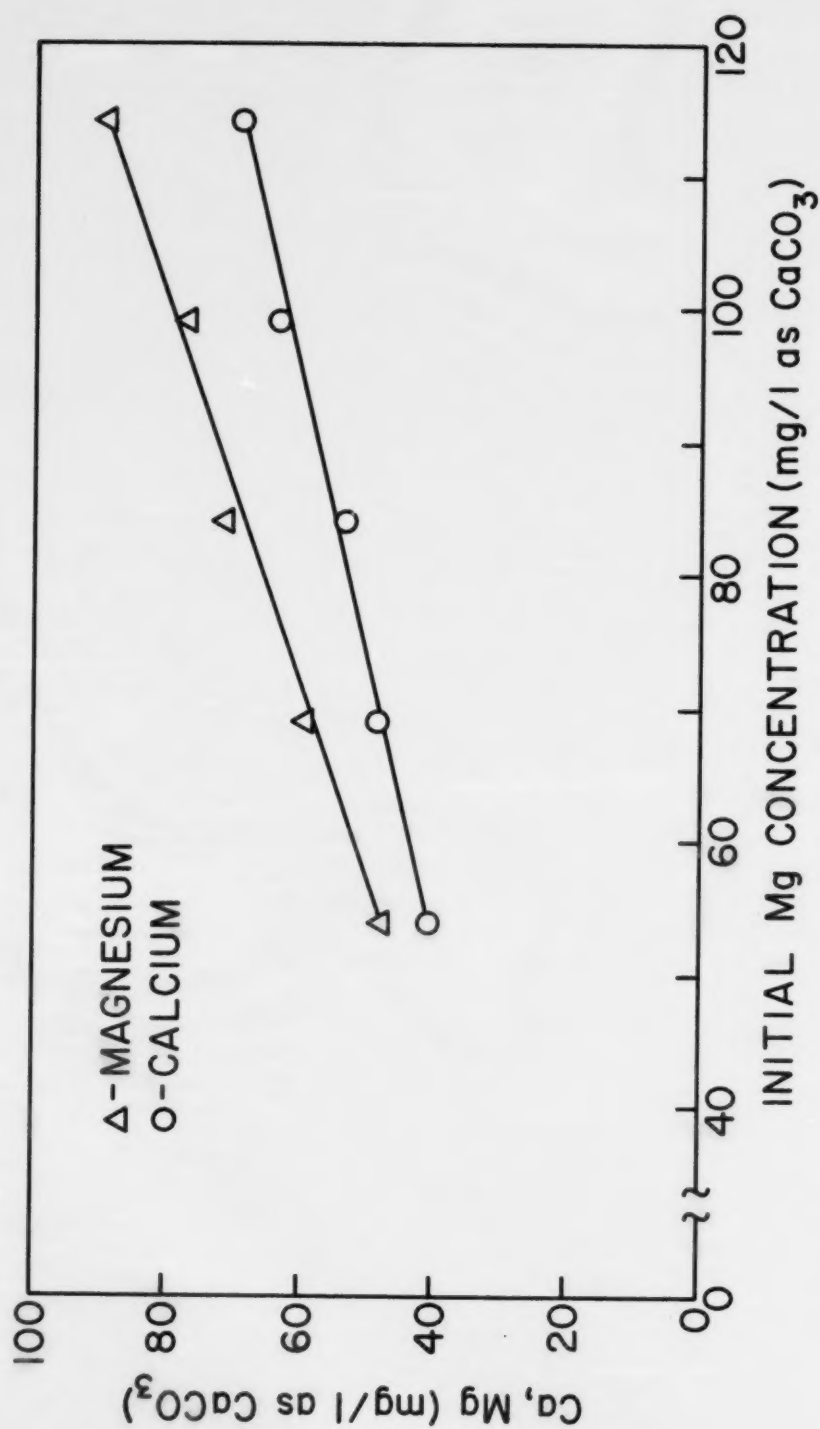


Figure 67. Effect of initial Mg concentration on Ca and Mg concentrations in treated Mississippi River water. pH = 10.9.

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Is not, therefore, clear what causes the improved removal at elevated pH. The increase in negative surface charge on the $Mg(OH)_2$ would suggest that surface absorption should decrease because of the increased electrostatic repulsion.

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The strong dependence of organics removal upon solution pH was also observed with lime addition as shown above in Figure 47. It is noteworthy that in Figure 47 the removal of organics (UVA) increased dramatically between pH 10 and 11.

Additional studies concerning the impact of the type of pretreatment on adsorption of organics by granular activated carbon columns are reported in Section 8 below.

8. Discussion

Black *et al.* (38,41) reported that color removal was most effective when waters high in magnesium were softened, and Steiner *et al.* (100) found that methoxychlor was best removed in the softening process at high pH and greatest $Mg(OH)_2$ precipitation. Idelovitch (99) also found pesticide removal was effective at high pH and claimed the pesticides were adsorbed onto $Mg(OH)_2$. However, these studies do not provide substantial evidence for a removal mechanism involving $Mg(OH)_2$. More recently, Randtke *et al.* (95) examined the removal of soluble organic contaminants and fulvic acids by lime-soda softening. In well-controlled experiments, Randtke was able to demonstrate that fulvic acids isolated from a local ground water were partially removed during softening. Removals were influenced by the amount of precipitate formed, the initial TOC, the pH and the presence of magnesium and phosphate ions.

Peat fulvic acid was removed by simply increasing solution pH in the presence of calcium. In the absence of carbonate ion, 40% of the fulvic acids was removed at pH 11 by precipitation. Similarly, in another carbonate-free study fulvic acid removal was observed to be a function of calcium concentration at pH 11.2. For example, no organics removal was observed in the absence of calcium and 40% removals were achieved for $[Ca^{++}] = 4mM$. This data suggested a precipitation mechanism and it is possible that a similar mechanism may exist with magnesium.

In this light, the observed increase in removals of organics observed at high pH may be explained by improved precipitation of the organics in the presence of calcium and magnesium. This explanation would also account for the data presented in Figure 66. Although the presence of magnesium improves the extent of organics removal, it is apparently not related to the amount of $Mg(OH)_2$ precipitate generated.

Randtke (95) also observed that with increasing initial TOC, the residual calcium hardness increased for a fixed lime dose. The increased organic content of the water was, therefore, complexing the calcium in a manner that prevented it from precipitating as $CaCO_3$ and yet the complex was not removed by filtration through a glass fiber filter. In this study the initial TOC of the river water was not a variable but the results of softening experiments with and without alum addition suggest that soluble Ca/Mg complexes are

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removed by alum addition. Alum addition not only improved the settleability of the sludge but it also improved hardness and organics removal. The very similar patterns in removals of UVA and hardness with alum dose suggest these parameters (UVA and hardness) are related and the additional hardness removed may be complexed with organics in the water. The mechanism by which alum brings about the precipitation of these complexes is not clear at this time.

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SECTION 7

A CHARACTERIZATION STUDY OF ORGANICS REMOVAL

INTRODUCTION

Water treatment facilities across the United States employ a variety of treatment processes for the production of potable water from local supplies. The choice of treatment process is determined by the quality of the source supply and the local treatment objectives. Lime softening is widely employed where hardness must be reduced to an acceptable level and this process can be successfully operated for the simultaneous reduction of color as is practiced in Minneapolis-St. Paul, Minnesota. Where the hardness of a water source is acceptable, chemical coagulation is usually employed to pretreat the water prior to filtration. The coagulation process is typically operated for turbidity removal and color removal if necessary.

Waters containing high organic content and color may, therefore, be treated effectively by both softening and coagulation. However, if a high level of organics removal is required for the reduction of THM precursors or because of the implementation of more stringent treatment standards, there is some question as to which process is most effective. Relatively little is currently known concerning the organic removal behavior of these processes.

In addition, the character of the organic compounds removed by lime softening and coagulation pretreatments has not been identified and compared. The purpose of the study reported in this section, therefore, was to employ a variety of chemical and physical characterization techniques to identify the changes in organic character that were wrought by chemical treatments and subsequent activated carbon treatment of a Mississippi River water sample.

Procedure

A 950 liter sample of Mississippi River water was collected and filtered through a trimedia filter as described in Section 3 of this report. The filtered Mississippi River water (FMRW) was divided into separate batches for various forms of treatment and analysis. The treatment and analysis scheme is depicted in Figure 68.

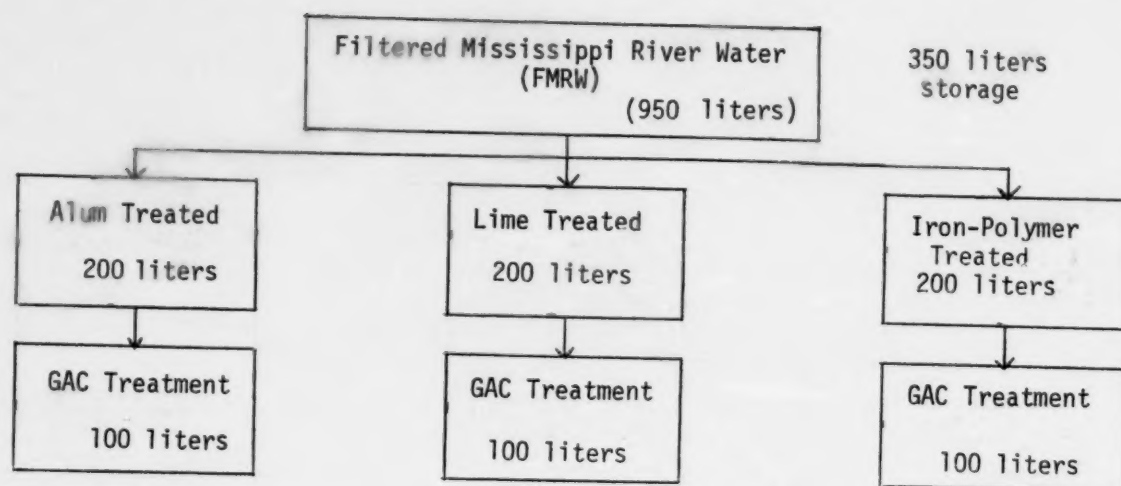
Approximately 200 liters of water were treated with lime and 60 liters of the product water was saved for analyses. The remaining water was treated by granular activated carbon (GAC) and 100 liters of the effluent water was saved for analyses. In a similar fashion 200 liter samples of river water were treated with alum and with iron and polymer. Sixty liter samples of the treated waters were saved and the remainder was treated by GAC to provide 100 liter effluent samples.

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Analytical: Molecular Weight Fractionation (MWF)
(Unchlorinated only) : TOC, TTHMFP.

Polarity Fractionation (PF)
TOC, TTHMFP.

Gas Chromatography/FID
Chlorinated
Unchlorinated

Figure 68. Sampling and analysis schematic for organic characterization studies.

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The extra river water collected was stored at 4°C as a safety precaution in the case of sample loss. Treatment studies were conducted on the water sample to evaluate the dose-response behavior of the sample and identify the chemical doses that should be used in this study. Coagulation jar test studies were conducted using UVA as an indicator of organics removal. The results are plotted in Figure 69 and 70. Figure 69 shows the UVA removal efficiency for alum and ferric sulphate alone, while Figure 70 shows the impact of a selected polymer, Arco 6320 P, when used in conjunction with ferric sulphate. An alum dose of 80 mg/L and iron dose of 20 mg/L with 3 mg/L of polymer were selected for study. These doses gave comparable removals of approximately 60-70% and little benefit was observed with larger coagulant doses. The choice of polymer was based upon test results for this polymer reported in Section 5 of this report.

A lime softening study was also conducted and the results are reported in Figure 71. The lime dose selected for study was 233 mg/L as CaCO_3 . This dose was based upon a standard bar graph analysis (34) to achieve a desired level of hardness of 80 mg/L as CaCO_3 . In this study the lime treated water was recarbonated. Recarbonation was affected by NaHCO_3 addition with a little H_2SO_4 added to reduce the pH to 9.0.

The effectiveness of the treatment processes when applied on a large scale (as described in Section 2 for the column study pretreatment procedures) to the FMRW is documented in Table 5.

TABLE 5. REMOVAL PERFORMANCE OBTAINED FOLLOWING LARGE-SCALE PRETREATMENT

	TOC		UVA	
	mg/L	% removal	abs	% removal
Alum Treated	2.86	52%	0.247	71%
Iron & Polymer	3.27	47%	0.29	65%
Lime & Recarbonation	4.21	33%	0.406	52%
FMRW Control	6.3	—	0.840	—

All the values reported in Table 5 were obtained by analyses conducted on the pretreated water following filtration through a trimedia filter described in Section 3. Samples of the filtered pretreated water were saved for additional characterization.

The next phase of treatment involved passing the pretreated water samples through granular activated carbon (GAC) columns. It was decided that the columns should be designed to produce an effluent having an average concentration of 1 mg/L for all the pretreated waters. Activated carbon column performance is strongly influenced by the type and level of pretreatment provided. If comparisons were made between the organic content of carbon treated waters following different types of pretreatment, the levels of removal may

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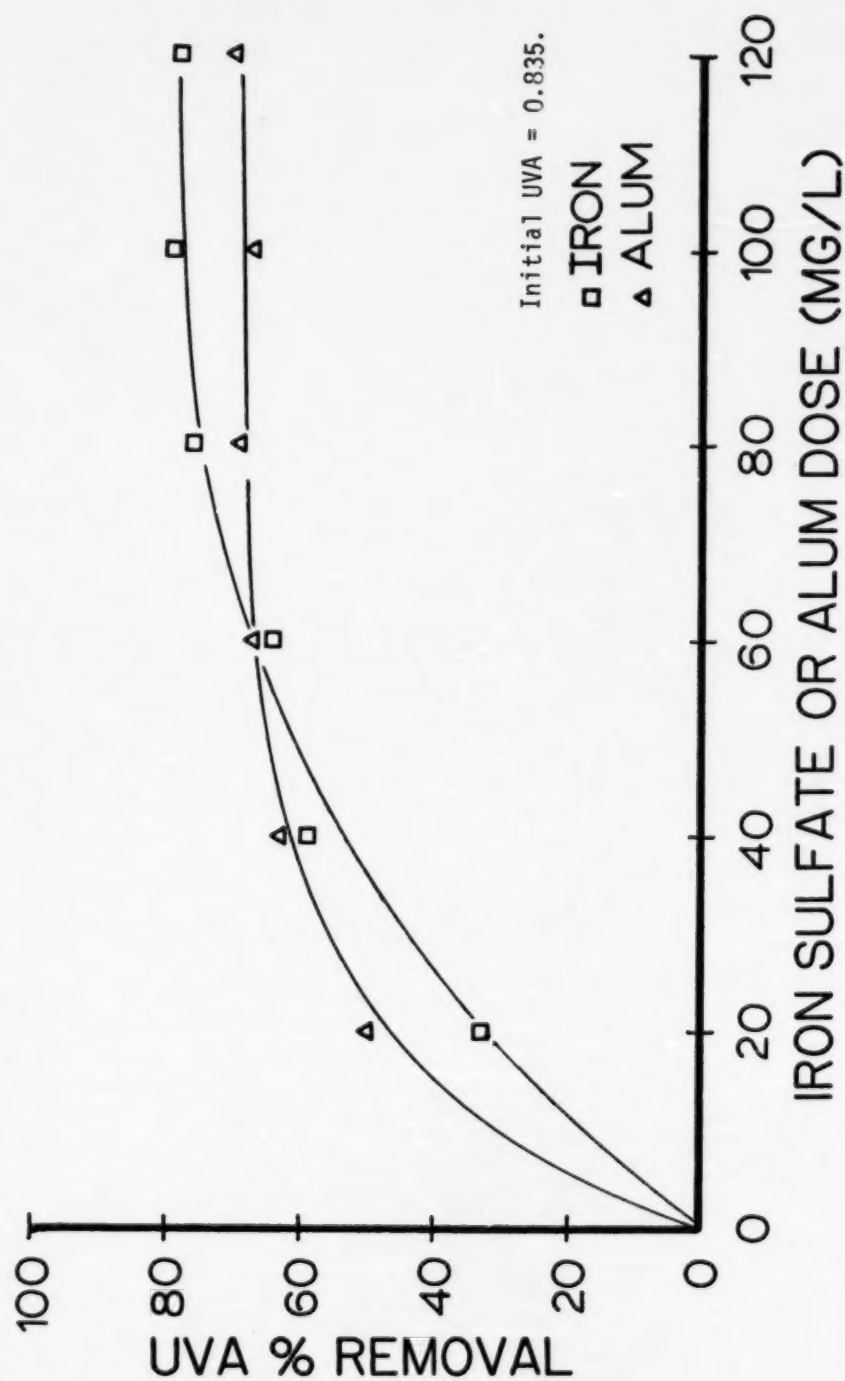


Figure 69. Jar Test Results to Evaluate Coagulant Dose Response of River Water Sample

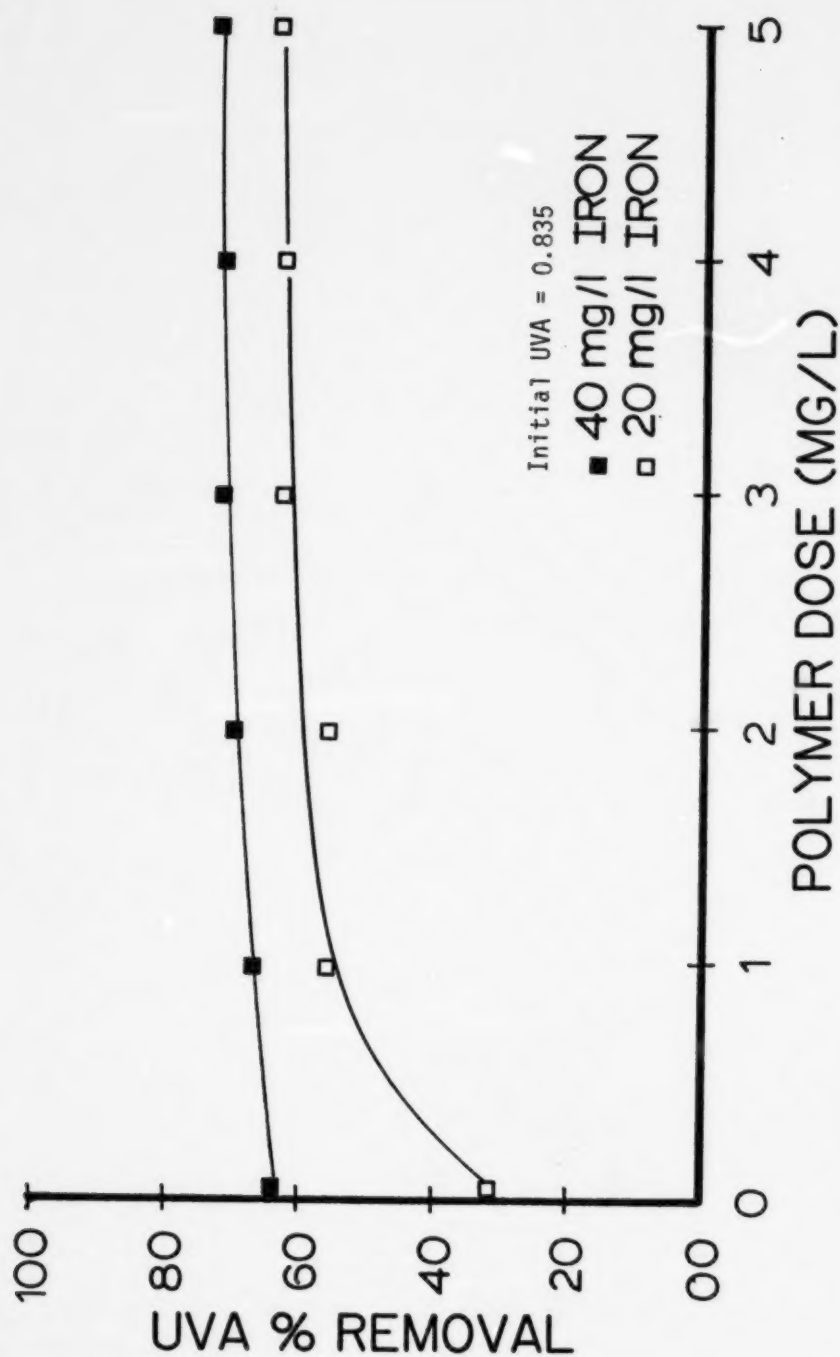


Figure 70. Influence of Polymer Addition on Coagulation of Mississippi River water with Ferric Sulphate.

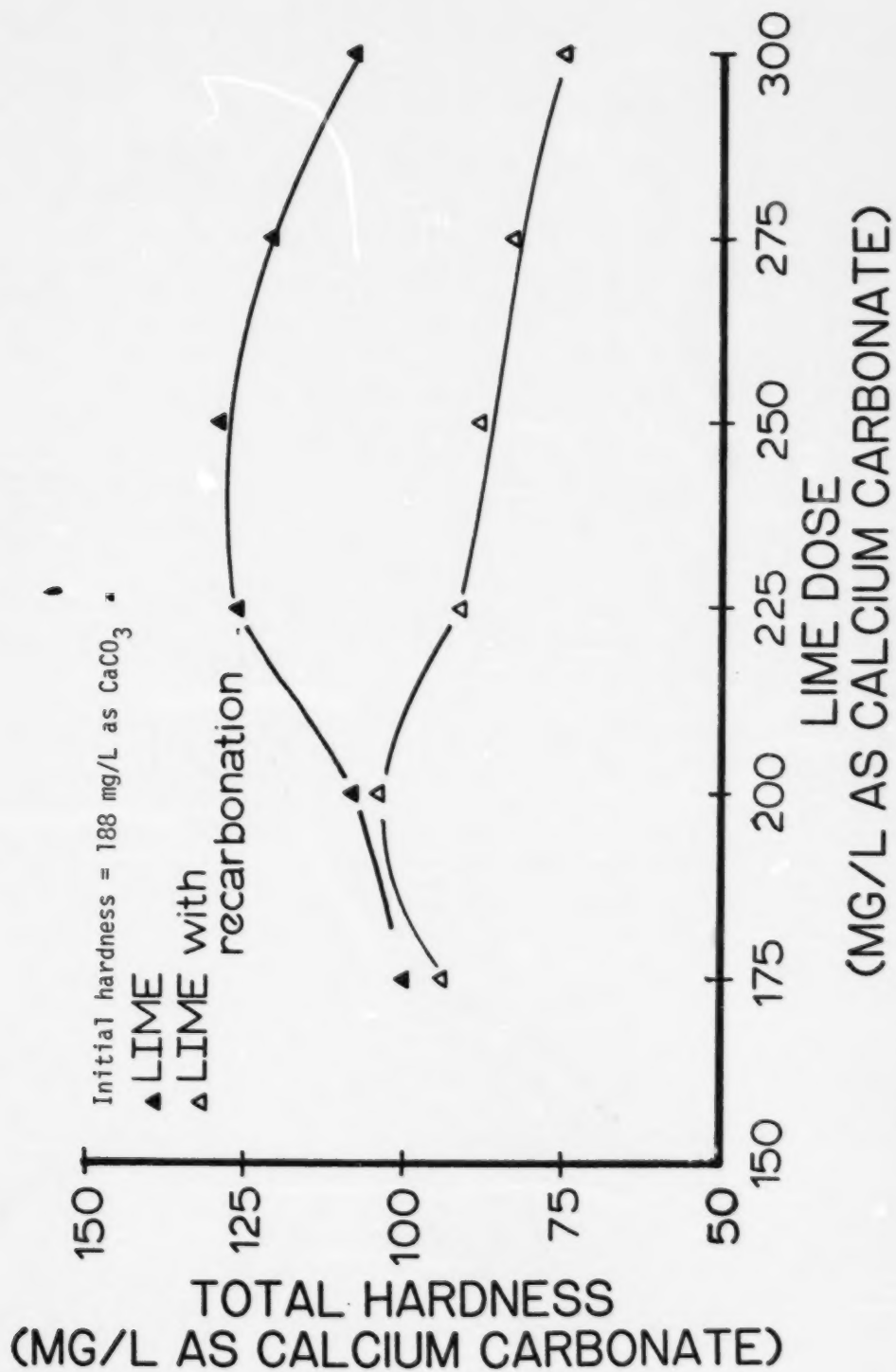


Figure 71. Influence of Lime Dose and Recarbonation on Hardness Removal from Mississippi River Water.

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not be equal. In such a case the comparison of effluent composition may not be valid since one column may be approaching exhaustion while another is still effectively reducing the influent organic content. To avoid this the carbon column dimensions were adjusted to provide an effluent of essentially constant quality for all the pretreated waters. Analysis of these effluents should, therefore, identify the nature of organics that are not effectively removed by activated carbon following different types of pretreatment.

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An examination of the experimental column results presented in Section 8 provided estimates of the carbon depths required. Two columns each containing a carbon bed 19.1 cm deep were prepared for the lime softened water sample, two 11.7 cm and two 14.4 cm carbon beds were prepared for the alum treated and iron-polymer (FeP) treated waters, respectively. At a flowrate of 3.5 mL/min these carbon depths provided empty bed contact times (EBCT) of 3.6, 2.2 and 2.7 mins, respectively.

The character of the breakthrough curves obtained for TOC and UVA are presented in Figures 72 and 73, respectively. All water samples were adjusted to pH 7 prior to GAC treatment to ensure that any differences in the character of organics removed from the various water samples were not attributable to the different operating conditions. The curves show more scatter in the data than many of the curves reported in Section 8 of this report. The scatter was probably attributable to frequent backwashing. Backwashing was practiced more frequently in these particular column runs to avoid any plugging or the possibility of improved removal because of superior filtration for any of the samples. In addition, since it appeared that the lime treated water might break through prematurely, the bed depth in the columns receiving lime treated water was increased by 5 cm on day 10 of the run. The measured TOC's of the blended effluents after 12 days were as follows: 0.98 mg/L for alum pretreatment, 1.06 mg/L for iron-polymer, and 1.17 mg/L for lime.

The treated water samples so prepared were characterized in detail and the results are presented below.

Polarity Fractionation

The polarity fractionation procedure employed in this study was developed by Leenheer and Huffman (33). In this procedure soluble organic carbon, measured by TOC analyses, is fractionated by macroreticular resins into acid, base and neutral hydrophobic organic solute fractions, and into acid, base and neutral hydrophilic organic solute fractions. The hydrophobic solutes are defined as those which adsorb onto non-ionic, non-polar resins (Rohm and Haas, XAD 2 and XAD 8) and which may be fractionated using these resins. The hydrophilic solutes are sorbed and fractionated by macroreticular ion exchange resins. By measuring the changes in sample TOC following contact with these resins under different pH conditions and by eluting adsorbed organics from the resins, as shown in Figure 3 the organic content of a water sample may be fractionated according to its sorptive character.

The basis for this fractionation was discussed in detail by Leenheer and Huffman (33). This fractionation scheme "fills a gap in organic solute char-

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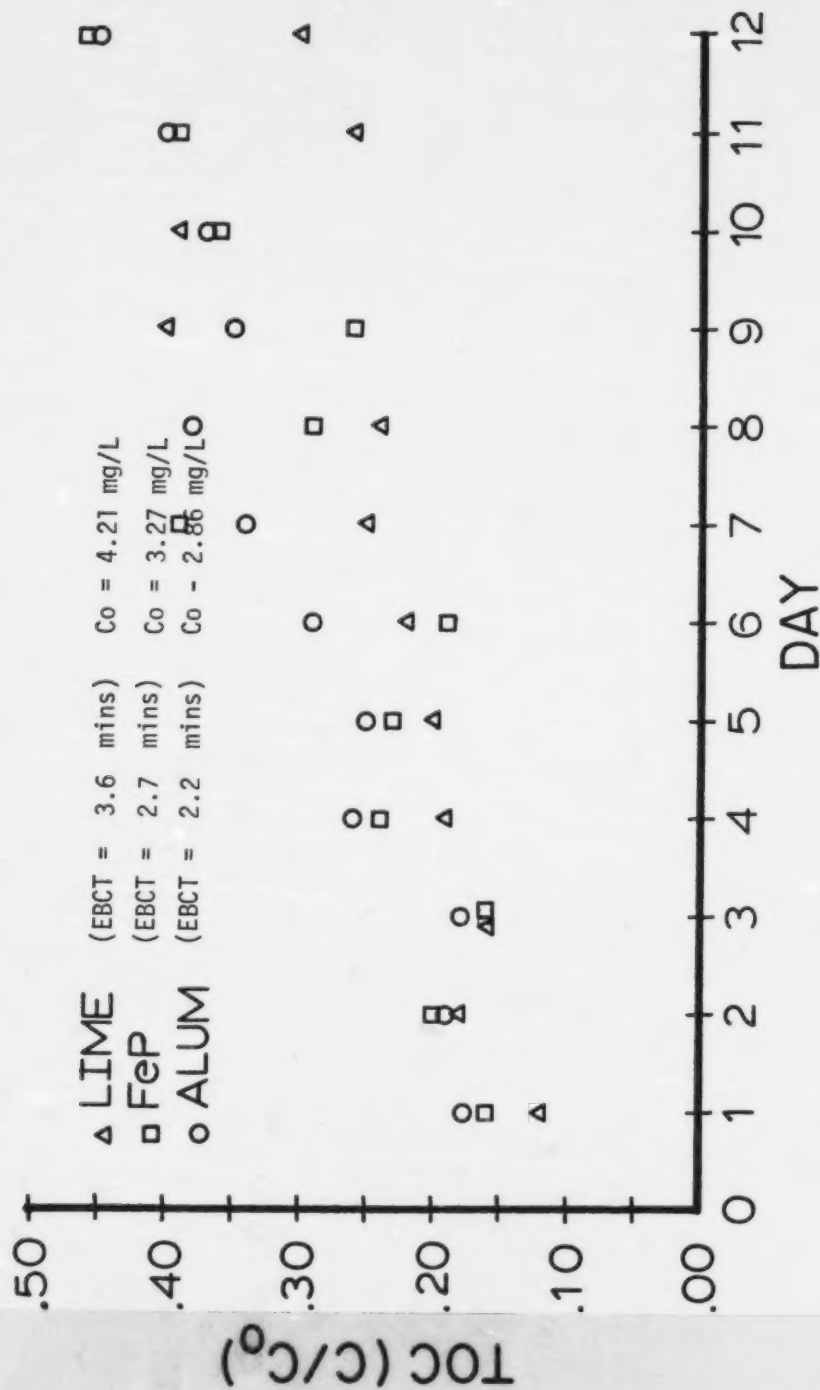


Figure 72. TOC removal from treated river water in GAC columns at pH 7.



Figure 73. UVA removal from treated river water with GAC treatment at pH 7.

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acterization between the organic solute concentration (TOC) and specific compound identification" (33). It must be recognized, however, that in the ensuing discussion of results, fractions are referred to as hydrophobic or hydrophilic, etc. These fractions are operationally defined for the conditions employed in the fractionation scheme.

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The polarity fractionation procedure as outlined in Section 3 was applied to each of the treated water samples and the river water control. The results are presented in Table 6. In addition, the data contained in Table 6 was selectively reduced in Tables 7 and 8 for clarity and ease of interpretation.

The fractionation of the river water sample indicated that 40% of the organic content was characterized as hydrophobic and 60% was hydrophilic. The hydrophobic fraction was predominantly acidic (63%) and neutral (35%) in character. By comparison, the hydrophilic content was mainly neutral (73%) and the acidic compounds only accounted for 17% organic content of this fraction. In both fractions the organic bases accounted for very little of the TOC.

The high concentration of neutrals and the low concentration of acids in the hydrophilic fraction was surprising. In reviewing the technique it became apparent that the exchange capacity of the anion exchanger was exceeded during the fractionation procedure and this caused organic acids to break through the resin and thus be measured as neutrals. As a result the fractionation procedure did not accurately distinguish between the hydrophilic acid and neutral fractions. The data presented in the tables below represent the organic content measured in each fraction and it was not possible to correct the data to identify the actual neutral and acid components. The data is presented for completeness but in discussion the hydrophilic neutrals and acids will be referred to as a single fraction.

Treatment of the river water sample by either lime or coagulation caused a reduction in TOC mainly by reducing the concentration of the acidic and neutral organic fractions. All treatments completely removed the hydrophilic base fraction, but the small original concentration of this fraction reduced the significance of this. Analysis of Table 7 reveals that the treatment processes removed the hydrophobic organic content somewhat better on a percentage basis, although a greater concentration of hydrophilic compounds were removed based upon the measured TOC values.

As shown in Table 6 the alum treated water showed the best TOC removal with iron-polymer treatment a close second. Lime showed the poorest removal. From the polarity fractionation data it was apparent that the lime was not as effective, at the applied dose, in reducing the acidic and neutral fractions to the same extent as alum. Coagulation with the alum and coagulation with iron-polymer gave essentially identical removal performance.

The granular activated carbon column treatment of the pretreated waters produced effluents which were essentially identical in quality and character. Regardless of the water pretreatment conditions, analysis of the carbon column effluent indicated that 70-80% of the organic compounds passing through the carbon were neutral in character and predominantly hydrophilic.

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TABLE 6. POLARITY FRACTIONATION STUDY TOC VALUES

Sample Description	Whole Sample	Polarity Fraction TOC (mg/L)					
		Hydrophobic			Hydrophilic**		
		Base	Acid	Neutral	Base	Acid	Neutral
Filtered River Water	6.27	0.05	1.57	0.87	0.36	0.66	2.76
Lime Treated	4.21	0.18	1.06	0.32	0.00	0.51	2.14
Fe-P Treated	3.27	0.05	0.71	0.36	0.08	0.03	2.04
Alum Treated	2.86	0.05	0.71	0.20	0.10	0.00	1.87
Lime + GAC *(EBCT = 3.6 mins)	0.95	0.01	0.06	0.12	0.03	0.03	0.70
Fe-P + GAC (EBCT = 2.7 mins)	0.90	0.01	0.05	0.09	0.10	0.01	0.64
Alum + GAC (EBCT = 2.2 mins)	0.92	0.01	0.04	0.14	0.10	0.01	0.62

*EBCT = empty bed contact time.

**The measurements of the hydrophilic acid and neutral fractions are inaccurate. (See text pg. 122).

TABLE 7. FRACTIONATION STUDY TOC VALUES
--COMPARISON OF HYDROPHOBIC AND HYDROPHILIC FRACTIONS

Sample Description	Polarity Fraction TOC mg/L		
	Hydrophobic	Hydrophilic	Ratio*
Filtered River Water	2.49	3.78	1.52
Lime Treated	1.56	2.65	1.70
Fe-P Treated	1.12	2.15	1.92
Alum Treated	.96	1.97	2.05
Lime + GAC (EBCT = 3.6 mins)	.19	.76	4.00
Fe-P + GAC (EBCT = 2.7 mins)	.15	.75	5.00
Alum + GAC (EBCT = 2.2 mins)	.19	.64	3.37

*Ratio = hydrophilic fraction/hydrophobic fraction.

TABLE 8. POLARITY FRACTIONATION STUDY TOC VALUES
--COMPARISON OF ACID, BASE AND NEUTRAL FRACTIONS *

Sample Description	Polarity Fraction TOC (mg/L)		
	Acid	Base	Neutral
Filtered River Water	2.23	0.41	3.63
Lime Treated	1.57	0.18	2.46
Fe-P Treated	0.74	0.13	2.40
Alum Treated	0.71	0.15	2.07
Lime + GAC (EBCT = 3.6 mins.)	0.09	0.04	0.82
Fe-P + GAC (EBCT = 2.7 mins.)	0.06	0.15	0.73
Alum + GAC (EBCT = 2.2 mins.)	0.05	0.11	0.76

*The measurements of the hydrophilic acid and neutral fractions are inaccurate. (See text pg. 122).

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The acidic and basic organic fractions were almost totally removed by carbon treatment. One should bear in mind the treatment objective in the design of the carbon column study. The lime pretreated water required almost twice the depth of carbon to achieve the same level of effluent quality (an average of 1 mg/L). This, therefore, suggests that the hydrophobic and hydrophilic acids and neutrals present in higher concentrations in the lime pretreated water were responsible for the earlier breakthrough. This is discussed in more detail below.

The fractionated samples of water were also analyzed for THM precursors following the measurement procedure described in Section 3. NaOH and H₂SO₄ eluates were diluted back to their equivalent river water volume using Milli-Q water. The dilution ratio was equal to the volume of river water treated by the resin column divided by the volume of eluate collected. Analyses conducted on the various water samples and their fractions are shown in Tables 9 to 11.

Analysis of the data contained in these tables indicates that in the raw river water the THM precursors were almost evenly split between the hydrophobic and hydrophilic fractions (47% vs. 53%). In addition, acidic and neutral fractions of the sample accounted for the majority of the organic content while the organic base fraction contributed a negligible amount. The negative numbers in Table 9 are caused by the computation technique employed and also perhaps by the fractionation scheme itself. For example, hydrophobic neutrals are calculated by subtracting three THM measurements from the THM concentration of the initial water sample. The accuracy of the hydrophobic base fraction is the poorest of those reported. All the other fractions were measured directly or by the subtraction of only two THM values. Negative values were also obtained for hydrophilic acidic and base fractions and this resulted from a situation where the ion exchange column effluents were higher in THM precursors than their respective feeds. This problem was consistent enough, especially for the cation exchange column (hydrophilic bases), that it cannot be simply dismissed as experimental error. It is likely that the use of an acid form cation exchange resin may actually alter the nature of the organic content slightly, making it more susceptible to THM production. The effect is very slight, but the extremely low internal pH of the cation exchanger and the elevated internal ionic strength may encourage hydrolysis or alter the configuration of the polymeric humic macromolecules in such a way that THM production increases. The effect was relatively minor and since little TOC was measured in the hydrophilic base fraction, the negative results were interpreted as being equivalent to zero THM production for this fraction. However, it must be recognized that this effect would cause an apparent increase in the concentration of hydrophilic neutral precursors.

As noted below, the mass balances on precursor concentrations were excellent and the total precursor concentration was not observed to increase as a result of the fractionation procedure.

Pretreatment caused approximately a 70% decrease in THM precursors in the hydrophobic fraction and a 40-50% decrease in hydrophilic precursors. As shown in Table 10 the selective removal of hydrophobic THM precursors caused

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TABLE 9. POLARITY FRACTIONATION STUDY TTHM VALUES

Sample Description	Whole Sample	Polarity Fraction TTHM (ug/L)						
		Hydrophobic			Hydrophilic *			
		Base	Acid	Neutral	Base	Acid	Neutral	
Filtered Water	456	3	119	84	-13	77	186	
Lime Treated	211	0	37	17	12	31	114	
Fe-P Treated	193	4	57	-4	-7	13	130	
Alum Treated	189	8	63	-2	-13	-7	140	
Lime + GAC (EBCT = 3.6 mins)	47	0	0	25	-15	0	37	
Fe-P + GAC (EBCT = 2.7 mins)	31	8	4	-11	-6	-2	38	
Alum + GAC (EBCT = 2.2 mins)	30	0	0	-5	-3	-2	40	

*The measurements of the hydrophilic acid and neutral fractions are inaccurate. (See text pg. 122).

TABLE 10. POLARITY FRACTIONATION STUDY TTHM VALUES
 --COMPARISON OF HYDROPHOBIC AND HYDROPHILIC FRACTIONS

Sample Description	Polarity Fraction TTHM (ug/L)		
	Hydrophobic	Hydrophilic	Ratio*
Filtered River Water	206	250	1.21
Lime Treated	54	157	2.91
Fe-P Treated	57	136	2.52
Alum Treated	69	120	1.74
Lime + GAC (EBCT = 3.6 mins)	25	22	0.88
Fe-P + GAC (EBCT = 2.7 mins)	1	30	30.00
Alum + GAC (EBCT = 2.2 mins)	-5	35	-

*Ratio = hydrophilic fraction/hydrophobic fraction.

TABLE 11. POLARITY FRACTIONATION STUDY TTHM VALUES
 --COMPARISON OF ACID, BASE AND NEUTRAL FRACTIONS*

Sample Description	Polarity Fraction TTHM (ug/L)		
	Acid	Base	Neutral
Sample River Water	213	-10	270
Lime Treated	68	12	131
Fe-P Treated	70	-3	126
Alum Treated	56	-5	138
Lime + GAC (EBCT = 3.6 mins)	0	-15	62
Fe-P + GAC (EBCT = 2.7 mins)	2	2	37
Alum + GAC (EBCT = 2.2 mins)	8	13	35

*The measurements of the hydrophilic acid and neutral fractions are inaccurate. (See text pg. 122).

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the ratio of hydrophilic/hydrophobic precursors to increase significantly. A more detailed analysis of the individual pretreatments may be made by inspection of Table 9.

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Surprisingly, the total THM precursor concentration in each of the pretreated samples was very similar and in the range of 189-211 $\mu\text{g/L}$. The sum of the THM precursors in the sample fractions ranged between only 204 and 211 $\mu\text{g/L}$. The overall mass balance was, therefore, excellent.

The iron-polymer and alum treated waters were essentially identical in character and generated approximately equal THM concentrations in each fraction. The lime treated water, however, showed a marked difference in character and THM precursor distribution. THM precursors in the lime pretreated water were found in the hydrophobic neutral, and the hydrophilic base fractions in higher concentrations than for the coagulated waters. This was compensated for a lower hydrophobic acid fraction such that the total THM production was roughly the same as the other pretreated waters.

The activated carbon treated water analysis revealed that the lime pretreated water gave the highest THM concentration following chlorination. The results of the fractionation for the lime-carbon treatment showed a significant precursor concentration attributable to the hydrophobic neutral fraction which was consistent with the influent water. Apart from this observation, the data in Table 9 suggest the THM precursor removal by carbon may be accounted for by the removal of hydrophobic acids and hydrophilic neutrals and organic acids.

Molecular Weight Fractionation

The results of the molecular weight fractionation study are presented in Table 12. The river water sample analysis revealed that 50% of the TOC was in the 1-10K fraction and 23% was less than 1K in size. The 10-100K and >100K fractions accounted for only 10% and 17%, respectively.

Analysis of the data in Table 12 indicates that all the pretreatments removed the 10-100K fraction of the TOC. In addition, all treatments reduced the >100K fraction to approximately 0.2 mg/L TOC. The effective difference between the pretreatments was apparent from their impact on the measured TOC's in the lower molecular weight fractions. Lime, iron-polymer and alum treatments reduced the TOC content of the 1-10K fraction by 52%, 57% and 68%, respectively. The coagulants did not cause any reduction in the fraction having a molecular weight less than 1000 nmw (1K). The lime pretreated water, however, actually caused a 40% increase in the low molecular weight (<1K) fraction. This may be explained if the lime treatment causes hydrolysis and a breakdown of the organic content in the higher molecular weight fractions.

For the activated carbon effluents the distribution of TOC among the molecular weight fractions was essentially constant. Approximately 70% of the effluent TOC was attributable to the <1K fraction and approximately 25% was associated with the >100K fractions.

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TABLE 12. MOLECULAR WEIGHT FRACTIONATION STUDY TOC VALUES

Sample Description	TOC mg/L				
	MWF Fraction				
	<1K	1-10K	10-100K	>100K	Total
Filtered River Water	1.47	3.17	0.63	1.07	6.34
Lime Treated	2.07	1.53	0.08	0.23	3.91
Fe-P Treated	1.48	1.37	0.00	0.22	3.07
Alum Treated	1.53	1.03	0.00	0.16	2.72
Lime + GAC (EBCT = 3.6 mins)	0.46	0.09	0.02	0.16	0.73
Fe-P + GAC (EBCT = 2.7 mins)	0.51	0.00	0.00	0.18	0.69
Alum + GAC (EBCT = 2.2 mins)	0.47	0.02	0.02	0.16	0.69

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The measured molecular weight distribution of the river water agrees with the observations of earlier investigators. Eisenreich *et al.* (47) measured the molecular weight distribution of dissolved organic carbon in a Mississippi River water sample drawn at St. Anthony Falls (the same location employed in this study). Using a similar membrane separation technique, they found that the distribution of TOC gave 70% less than 10K, 15% in the range 10-25K, 12% in the 25-100K and 2% greater than 100K.

The molecular weight distribution of the water was influenced significantly by coagulation with alum and iron. The higher molecular weight organics were more effectively removed by these hydrolyzing metal salts. This was anticipated since many previous studies provide evidence of this effect. For example, most of the organic color in surface waters is typically associated with the higher molecular weight humic acids (35) and color may be removed effectively by coagulation (36-39). In addition, higher molecular weight organic compounds in water are very large in size and their polyelectrolyte character provided by dissociated surface carboxylic, phenolic and ketonic functional groups allows them to be classified as colloidal particles (40). The separation of colloidal particles from water is the primary function of coagulation as it is practiced in conventional treatment facilities for turbidity removal. Several investigators have demonstrated a stoichiometry between the required coagulant dose and the concentration of humic/fulvic acids in a water sample for turbidity and color removal (38,41-43). This may be explained by a mechanism of adsorption of polymeric cationic aluminum or iron species at the organic surface with concomitant neutralization of the surface charge (28). The uncharged complexes may then flocculate/precipitate, depending upon their size, and be removed from solution. Several researchers have obtained results in studies on organics removal by coagulation that are best explained by the precipitation of aluminum or iron humates and fulvates (43,36).

For the lower molecular weight organic compounds some removal may also occur by processes such as the association of the "neutralized" metal-organic complexes with larger molecular weight species during the flocculation process. However, the smaller organic compounds may be sufficiently hydrophilic, that even if metal ions associate with their functional groups, they are not rendered insoluble and removed during coagulation (41).

Truly dissolved organic compounds may also be partially removed during the coagulation process (19-23) as discussed in Section 4 of this report. Removals occur by processes such as complexation, co-precipitation and adsorption to $Al(OH)_3$ or $Fe(OH)_3$ floc or to incorporated humic and fulvic acid surfaces. Removals of truly dissolved low molecular weight compounds are relatively small, however, as shown in Section 4.

Lime pretreatment has not been studied extensively in water treatment for its impact upon the removal of organics. Several studies have been conducted on color removal using lime treatment and these processes have been effective for color removal. However, very few studies have been conducted to identify the character of organic compounds removed by lime treatment. As discussed above, color is primarily associated with higher molecular weight organic acids and the removal of this molecular weight fraction by lime was therefore anticipated. However, the increase in TOC in the low molecular weight fraction was not anticipated. Molof and Zuckerman (44) reported that

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the lime treatment of wastewaters caused hydrolysis of high molecular weight organics and a shift in the molecular weight distribution towards lower molecular weight compounds. This controversial conclusion was contested in a discussion by Weber (112) who found no evidence of significant hydrolysis except for the breakdown of proteins. Using a technique of thin layer chromatography, protein hydrolysis was observed to occur when the sewage was held at pH values above 10 for several hours. However, this was judged to be a relatively minor effect and "hydrolysis tests" based upon altered adsorption characteristics gave no indication of any change in the character of organics in the wastewater.

In this study, the shift in TOC to the less than 1K fraction was significant. Hydrolytic breakdown of the organic compounds into smaller fragments is not necessarily the mechanism, however. It is possible that the high pH conditions alter the special configuration of the fulvic acid molecules in a manner that better affords them passage through the 1K membrane. Even though the solution pH was reduced to a constant level prior to membrane filtration, exposure to high pH values may have caused irreversible changes in organic character that encouraged the movement of a larger fraction of the organics through the 1K membrane.

It must also be remembered that the molecular weight characterization in this study is operationally defined by the character of the membranes and the conditions selected for study. Since the study was mainly comparative, the exact conditions tested are not of major importance. However, in explaining differences in observed molecular weight distributions, one should also recognize the limitations of the applied technique of estimating the molecular weight distribution.

Ultrafiltration membranes do not exclude all organic molecules with a molecular weight above their stated nominal molecular weight cut off. Molecular configuration, membrane character, operating pressure, pH, ionic strength, and degree of concentration in the retentate all influence membrane rejection and some higher molecular weight compounds may be able to pass the membrane while certain lower molecular weight molecules may be rejected.

During lime treatment the concentrations of calcium and magnesium ions were reduced and the ionic strength was decreased relative to the raw water sample and the coagulated samples. The reduced concentration of the divalent cations in solution may have, therefore, caused a change in the rejection efficiency of the 1K membrane for the organic content of the water.

The results of the fractionation study on the carbon treated water (pH = 7.0) indicate that some high molecular weight and some low molecular weight organics resisted removal by carbon under the conditions tested. This kind of behavior has been noted previously by several investigators. Certain low molecular weight polar organic compounds such as sugars, aliphatic acids and their salts, chlorinated hydrocarbons and phenolic compounds may not be removed very well by activated carbon (45,46,49), although they might well be biologically degraded, but 1 week was probably not enough time for organisms to become acclimated in this GAC test. These compounds are hydrophilic in

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character and adsorption capacities on activated carbon for these compounds are very low (15,46). Typically, the adsorption capacity of carbon for an organic compound increases as molecular weight increases for compounds in the same homologous series (15).

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Stevens et al. (48), employing gas chromatography to evaluate the organic removal effectiveness of activated carbon, noted that larger molecular weight, less volatile organic compounds eluting late during the gas chromatographic analysis were generally better removed than the more volatile early eluters. Chow and David (45) found that when they analyzed the character of organics resistant to adsorption during the treatment of wastewater, the compounds were small (less than 240 nm in dimension) and many of the compounds were biodegradable. Chian and DeWalle (49) observed that the major fraction of organics removed by activated carbon fell in the molecular weight range between 100 and 10,000 nominal molecular weight for studies in which carbon was applied to secondary effluents. Low molecular weight material (<100 nmw) was very poorly removed. However, the authors noted that there was evidence in their study to indicate that aerobic biodegradation of the low molecular weight compounds (<100 nmw) produces higher molecular weight, fulvic acid-like compounds which are well removed by carbon.

Chow and David also found that high molecular weight compounds (>100K nmw) were poorly removed by carbon and explained this observation by invoking "steric difficulty" during their entry into the subsequent diffusion within the carbon pores. Chian et al. (49) also noted that carbon was not effective in removing carbohydrate-like compounds having a molecular weight over approximately 50K.

It appears, therefore, that carbon removes a broad spectrum of organic compounds. However, carbon has a low adsorption capacity for low molecular weight hydrophilic organics. The polarity fractionation study indicated that ~70% of the organic compounds in the carbon column effluents were characterized as hydrophilic neutral compounds (Table 7) and only about 20% of the effluent organics were characterized as hydrophobic in character. The effluent TOC from each of the carbon columns was, therefore, primarily associated with low molecular weight hydrophilic compounds.

TTHMFP measurements were made upon the various molecular weight fractions for each of the water samples tested. The results are shown in Table 13. As Table 13 shows, some negative values were obtained in this analysis, but these values result from the mathematical manipulation of the data rather than experimental considerations. For example, the TTHMFP for the >100K fraction of the filtered Mississippi River water is recorded in Table 13 as -40. This result was obtained since the measured TTHM's in the 100K membrane filtrate exceeded the concentration found in the retentate. But since both numbers were large, the error associated with their difference was significant.

The data obtained were generally consistent and summation of the formation potentials in the individual fractions generally came within 10% of the value for the original water sample. The data are also consistent with the distribution of TOC among the different weight fractions as may be seen by comparing Tables 11 and 12.

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TABLE 13. MOLECULAR WEIGHT FRACTIONATION STUDY
--TTHMFP VALUES

Sample Description	TTHMFP ($\mu\text{g/L}$)				
	MWF Fraction				
	<1K	1-10K	10-100K	>100K	Total
Filtered River Water	82	225	30	-40	297
Lime Treated	104	84	-5	-29	154
Iron-Polymer Treatment	95	50	-1	-10	134
Alum Treatment	74	59	-1	1	133
Lime + GAC (EBCT = 3.6 mins)	14	12	-8	0	18
Fe-P + GAC (EBCT = 2.2 mins)	19	-2	-1	4	20
Alum + GAC	19	6	-3	-6	16

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The major contribution to THM production in the filtered river water sample was associated with the 1-10K molecular weight fraction (225 µg/L) and the <1K fraction contributed the next largest concentration of THM precursors (82 µg/L). The larger molecular weight fractions did not contribute significantly to THM production. Following all the treatments studied the high molecular weight precursors were reduced essentially to zero and precursor concentrations were limited to the two lowest molecular weight fractions.

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Lime pretreatment caused an apparent increase in the precursor concentration in the <1K fraction. This increase cannot be dismissed as experimental error since the reported concentration was measured directly and required no mathematical manipulation. In addition, the TOC was also observed to increase in this fraction for lime treated water as previously noted. A marginal increase in the <1K fraction was also noted for iron-polymer pretreatment. The TOC of this fraction, however, indicated that this pretreatment yielded no net TOC removal. The character of organics in this fraction may have changed slightly, however, since as Table 9 indicates, the character of organics in the product water differed significantly from the filtered river water sample. It is also possible that the polymer employed may have contributed to THM formation in the product water. Kaiser and Lawrence (50) found that chlorination of water samples containing commercially available polyelectrolytes produced chloroform. Their studies were conducted with 10 mg/L of CL_2 for four hours and thermal and ultraviolet excitation were employed to catalyze THM production. While their study suggested the production of chloroform was small, they found a variable response for different polyelectrolytes and the polymer used in this study was not evaluated. Furthermore, in this study the more stringent chlorination conditions (48 mg/L for 48 hours) may have caused the formation of greater concentrations of chloroform than those investigators found. Certainly, since there is a lack of information on the chemical composition of commercial PE formulations and their impurities, such as monomers and oligomers, their possible contribution to THM production cannot be overlooked.

Further examination of Table 13 reveals that lime treatment reduced the precursor concentration in the 1-10K fraction by 63%, whereas the coagulation pretreatments provided 74 and 78% removal of this fraction. Removals in the less than 1K fraction were negative for lime and iron-polymer, as discussed above and alum only yielded a very slight reduction in the precursor concentration from 82 to 74 µg/L in this fraction. It is apparent, therefore, that low molecular weight precursors are poorly removed by the pretreatment processes studied.

Analysis of the precursor concentrations in the carbon treated waters showed that the concentrations of precursors in the low molecular weight fractions were reduced dramatically (80-86%) and the concentrations in all the column effluents were very similar. Remember, however, that an average TOC of 1 mg/L was the goal of the GAC treatment.

GC/FID Fingerprinting

GC techniques are employed for the analysis of low molecular weight

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EPA Form 2350-4 (4-80)

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volatile organic compounds in a water sample. This portion of the TOC spectrum includes many of the synthetic organic chemicals (SOC's) as well as THM's, and the concentrations of all specific organic compounds regulated by maximum contaminant levels (MCL's) are measured by GC techniques. To accurately measure the concentration of a regulated organic in water the samples must be concentrated by techniques such as solvent extraction or the purge and trap procedure and analyzed on a GC equipped with an appropriate detector.

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In research studies on water treatment effectiveness one would like to learn as much as possible regarding the removal of specific organic compounds. Current techniques in computerized GC-Mass Spectrometry (GC/MS) provide quantitation and identification of all the peaks in a chromatogram generated from a solvent extract. These techniques, therefore, provide the best approach for identifying the removal behavior of processes such as activated carbon for specific organic compounds. However, the cost of completing this type of analysis is substantial since a great deal of work is involved in sample preparation, compound identification and quantitation, and also because the equipment required for these analyses is very expensive.

The GC fingerprint technique offers a qualitative assessment of organics removal for very much less cost. In this approach GC/Flame Ionization Detection (GC/FID) is employed to obtain a chromatographic profile of the organic content of a water. The organic compound "fingerprint" of the sample may then be compared with profiles obtained in other samples and the effectiveness of various treatment strategies may be discussed.

Popalisky et al. (52) first employed this type of approach at Kansas City in the early 1970's and correlated certain GC peaks with taste and odor problems. More recently Suffet et al. (53,54) have employed computers to simplify the presentation of packed and capillary column chromatographs and to make the comparison of data easier.

A recent paper by Stevens et al. (55) also discussed profile indexing methods employed to represent the chromatograms in reduced tabular form. However, these authors point out that much useful information may be lost by applying these data reduction techniques. They state that "In the Drinking Water Research Division Laboratories (EPA) "impressions" of the relative intensity of contamination are reached simply and directly by comparing the organic profiles of two or more extracts with no further data reduction." This approach was also employed in this study.

The results of the gas chromatography GC fingerprinting procedure described in Section 3 are presented below. The GC profiles represent impressions of relative concentrations of detected compounds in the river water and treated water samples (51). These profiles do not provide quantitative information concerning the water quality and the effectiveness of alternative treatment. Instead, they may provide an indication of treatment effectiveness when used in a comparative way.

The GC/FID procedure developed by Suffet et al. (56) and detailed in the same reference was evaluated for obtaining a "fingerprint" of the organic

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content of Upper Mississippi River water. However, the column packing recommended by these authors - 20% SE30 on 80/100 Gas Chrom Q caused an unacceptable level of column bleed and a satisfactory blank could not be obtained. Extensive conditioning of the column did not improve the column performance and, in addition, when sample extracts were tested, poorly defined peaks were obtained. For these reasons, several other packings were tested and 6% SE30 on 80/100 Gas Chrom Q was found to yield the best GC data. The GC profile obtained for an ether blank with this packing is shown in Figure 74. The output indicated that the ether caused a very large solvent peak which took a long time to return to the base line. Regardless of the operational conditions selected, the solvent peak could not be improved significantly and Figure 74 represents the curve obtained under the best conditions. Distinct peaks were noted at residence times of 9 minutes, 23.8 minutes and 28.5 minutes in the GC profile of the blank. However, many smaller blips were noted on the chromatogram as the solvent peak declined.

Because of the slow return to the baseline following the solvent peak, different attenuations were employed during each run to keep as many peaks on scale as possible. The attenuation changes are noted in each figure. Ideally, dual frame ionization detectors should have been used in this study since this would have allowed the solvent blank to be corrected out of the chromatogram. No funds were available for the purchase of a second detector, however.

To gain some insight into the character of compounds eluting at different retention times in this study, a selection of known compounds was injected with the ether blank. From the resulting GC profiles, the compounds' retention times were measured and the results are summarized in Table 14. The results provide some measure of the relative volatility of compounds eluting in the sample chromatograms. In addition, the profiles generated by Suffet *et al.* (56) provide some information on the character of compounds detected in the first 25 minutes of the chromatograms.

In all, seven water samples were tested to obtain GC/FID fingerprints. Each sample was tested with and without chlorination. The chlorination procedure employed is detailed in Section 2 of this report and care was taken to ensure that the excess chlorine was reduced prior to passing water samples through the XAD resin.

The samples of filtered Mississippi River water yielded the chromatograms shown in Figures 75 and 76. The peak retention times are reported as relative retention times (RRT) against 2 ethyl-1-hexanol which was employed as a standard. No internal standard was employed; however, 2-ethyl-1-hexanol was injected prior to each sample tested on the GC and the relative retention times are thus corrected for slight differences in operating conditions on different test dates.

Large peaks were noted at RRT's of 0.57, 1.59, 1.75 for the unchlorinated sample in Figure 75. When the sample was chlorinated, a very similar chromatogram was obtained, but the peak at 0.57 RRT was increased somewhat and an additional peak was noted at an RRT of 3.37.

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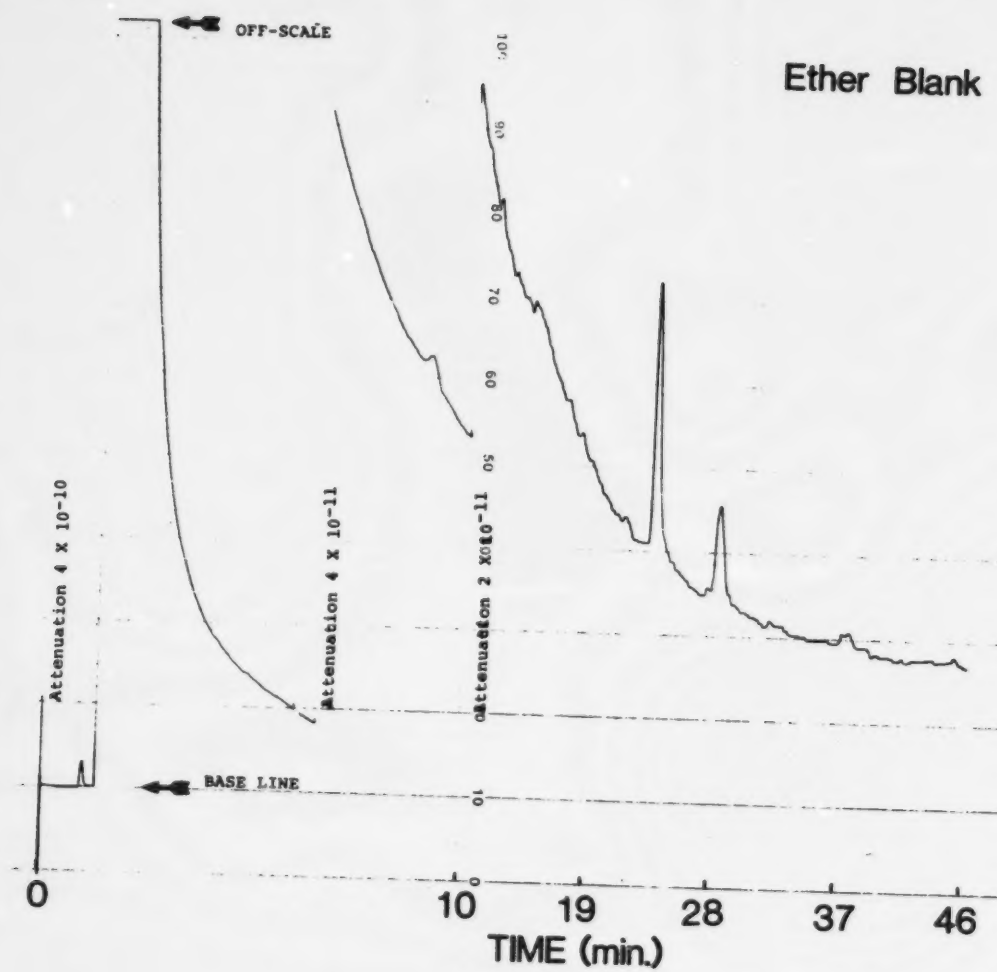


Figure 74. GC/FID analysis of an ether blank.

TABLE 14. RETENTION TIMES OF KNOWN COMPOUNDS
UNDER CONDITIONS TESTED IN GC/FID ANALYSIS

Compound	Retention Time RT (mins)	RT/RT _s *
chloroform	2.1	0.22
4 methyl 2 pentanone	4.2	0.44
phthalic acid	11.6-	1.27
benzene	3.2	0.34
biphenyl	15.4-	1.63
dichloromethane	--in solvent peak	
2,4,4' TCB	>45	4.76
2,4 DCB	43+	4.50
chlorophenol	12.1	1.27
formaldehyde	37-46+	3.87-4.82
p-nitrophenol	24	2.51
chlorobenzene	6.1	0.64
1,2 dichloroethane	2.9	0.3
phenol	35.4	3.71
cyclohexarone	6.9	0.72
benzaldehyde	8.1	0.85
nitrobenzene	10.5	1.10
dibutyl-pthalate	30.4	3.18
benzophenone	19.3	2.02
dinonyl pthalate	15.3	1.60
2 ethyl-1-hexanol	9.5	1.00

*Retention time relative to 2 ethyl 1 hexanol

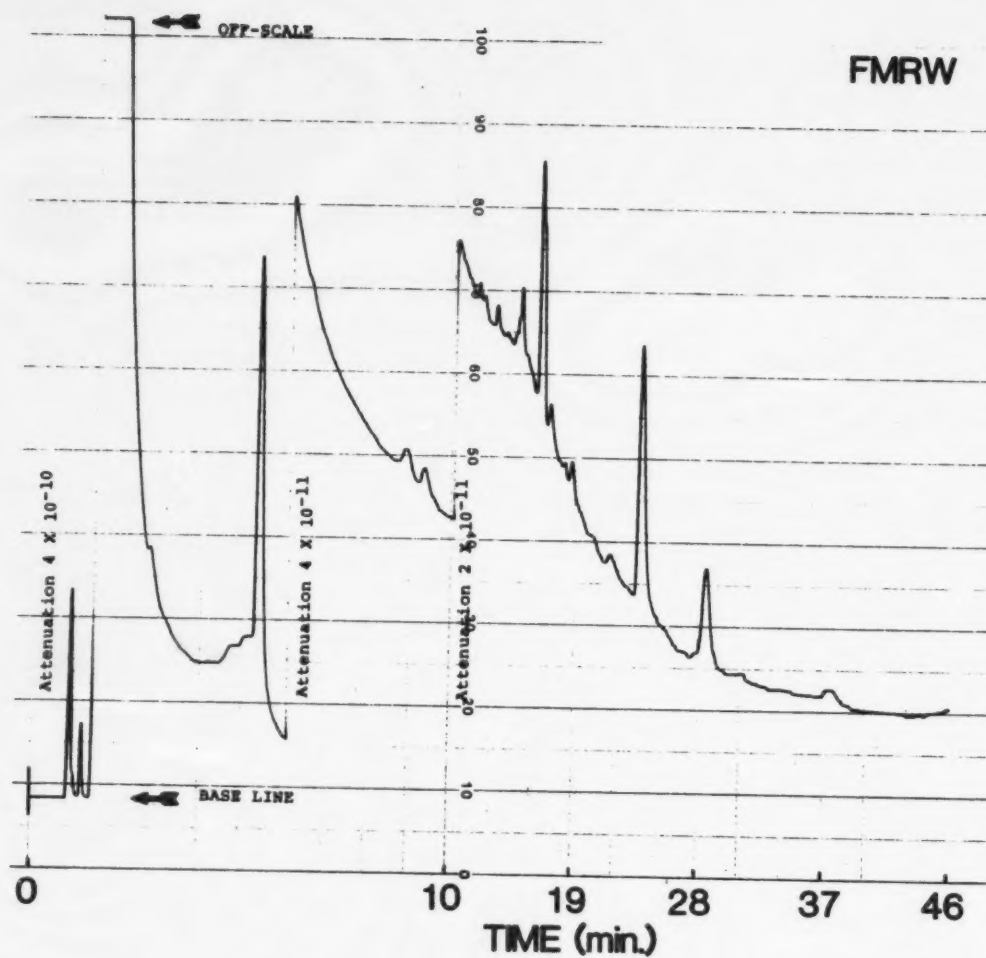


Figure 75. GC/FID analysis of filtered Mississippi River water.

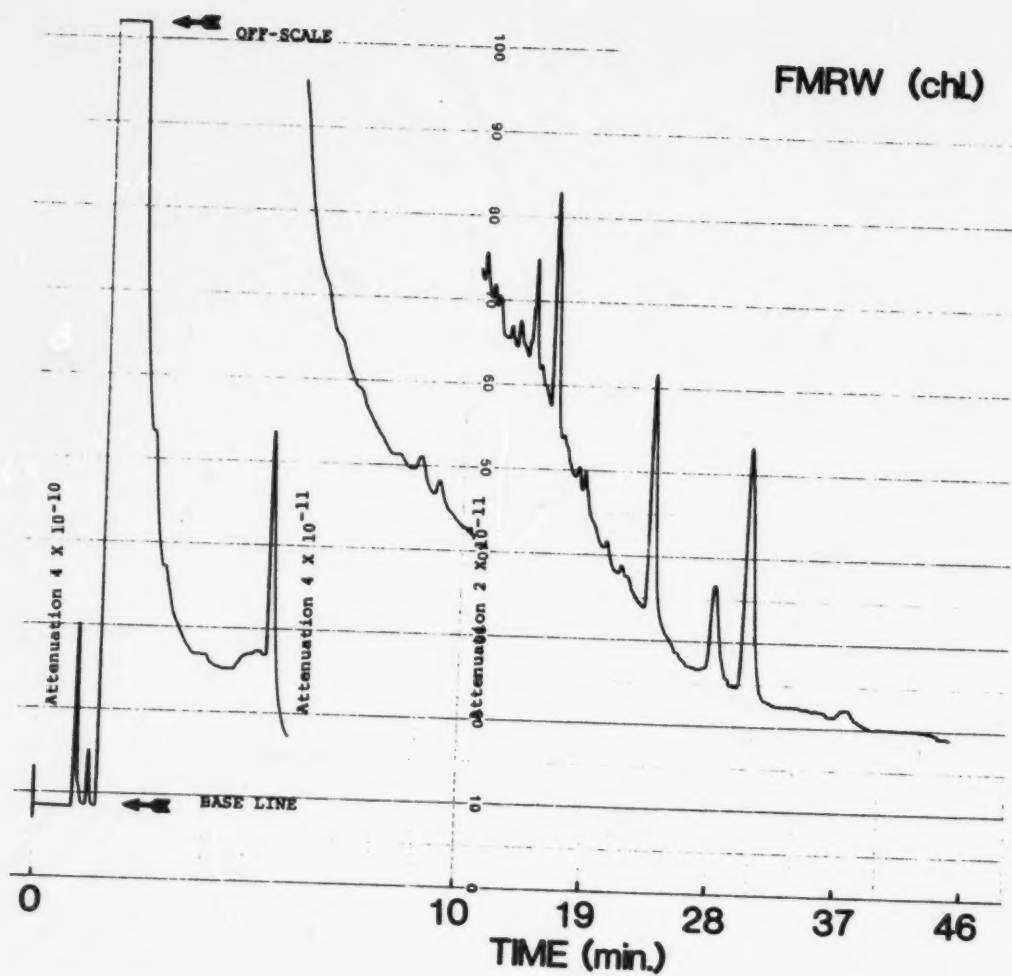


Figure 76. GC/FID analysis of chlorinated filtered Mississippi River water.

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Chlorination can produce acids which will not elute through a GC column, or it can reduce a compound sensitivity toward FID by adding polar groups (111). These peaks may be chlorinated products and known compounds that elute at $RRT = 0.57$ include chlorobenzene and trichloroacetone. Trichloroacetone was detected and identified in river water samples tested by Suffet *et al.* (56). The chlorinated product at $RRT = 3.36$ is a much less volatile compound and it is possibly a chlorinated aromatic organic compound.

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The lime treated water samples generated the chromatograms in Figures 77 and 78. The lime treated water samples gave exactly the same profiles as the other pretreated water samples. Significant peaks were observed in the lime pretreated unchlorinated sample at RRT 's of 0.57, 0.97, 1.27, 1.44, 1.57, 1.71, 1.79, 1.96, 3.97. The large numbers of chromatographable compounds identified in the pretreated water sample compared to the river water may have resulted from the different volumes of water sampled (river water -10 liters, pretreated water 20 liters and GAC treated water 40 liters) or perhaps from altered adsorption behavior of the XAD resin in the different water samples. Considering the latter possibility first, it was thought that perhaps the high concentration of higher molecular weight organics present in the river water may adsorb in preference to the lower molecular weight compounds that could be detected by the GC/FID technique. This possibility was unlikely, however, since the small volume (10 liters, 870 bed volumes) of water treated was unlikely to have exhausted the resins adsorption capacity or caused significant displacement of lower molecular weight organics. Close comparison of Figures 77 and 75 suggest that the difference between the two profiles stems from the volume of water extracted.

All of the peaks in Figure 77 are present in Figure 75 but many are ill-defined in the river water sample. When the volume of water extracted was increased, these peaks were better defined and distinguishable from the background noise in the chromatogram. In this regard, it was apparent that the pretreatment processes did not alter the observed organic profile significantly and this was to be expected. Earlier studies presented in this report indicate that higher molecular weight organics were primarily removed during pretreatment and the lower molecular weight chromatographable compounds were not significantly affected.

Chlorination of the pretreated water did not alter the organic profile obtained with lime only. However, the peaks corresponding to RRT 's of 0.57 and 0.97 were significantly reduced. Comparing this response to chlorination with the response of the river water, it is interesting to note that the chlorination of river water increased the peak at $RRT = 0.57$. Furthermore, the large peak produced in the river water at $RRT = 3.37$ was not generated in the pretreated water samples.

The alum pretreated chromatograms are shown in Figures 79 and 80 and essentially show exactly the same results as discussed above for lime treatment. The samples pretreated with iron and polymer were also tested and the chromatograms were similar to those obtained with lime and alum. The results for iron + polymer are shown in Figures 81 and 82.

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The GC/FID profiles of the carbon treated water for lime pretreatment

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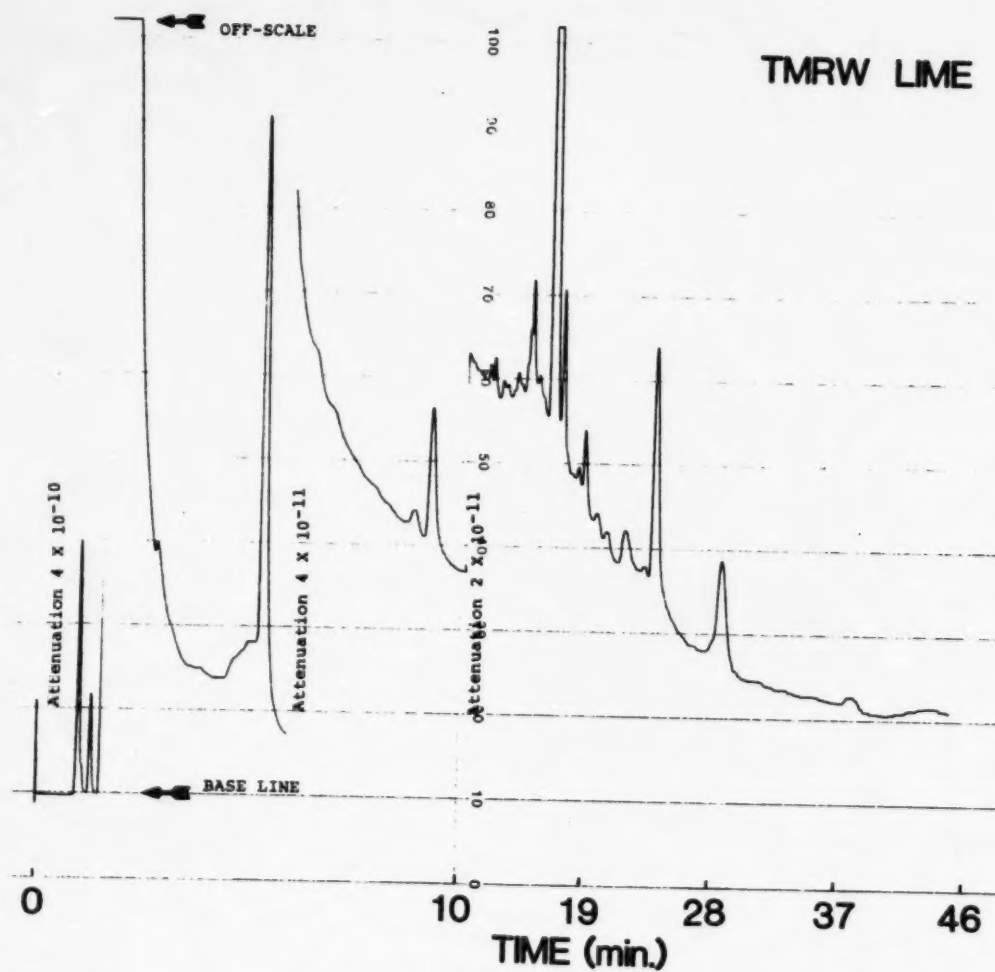


Figure 77. GC/FID analysis of lime treated Mississippi River water.

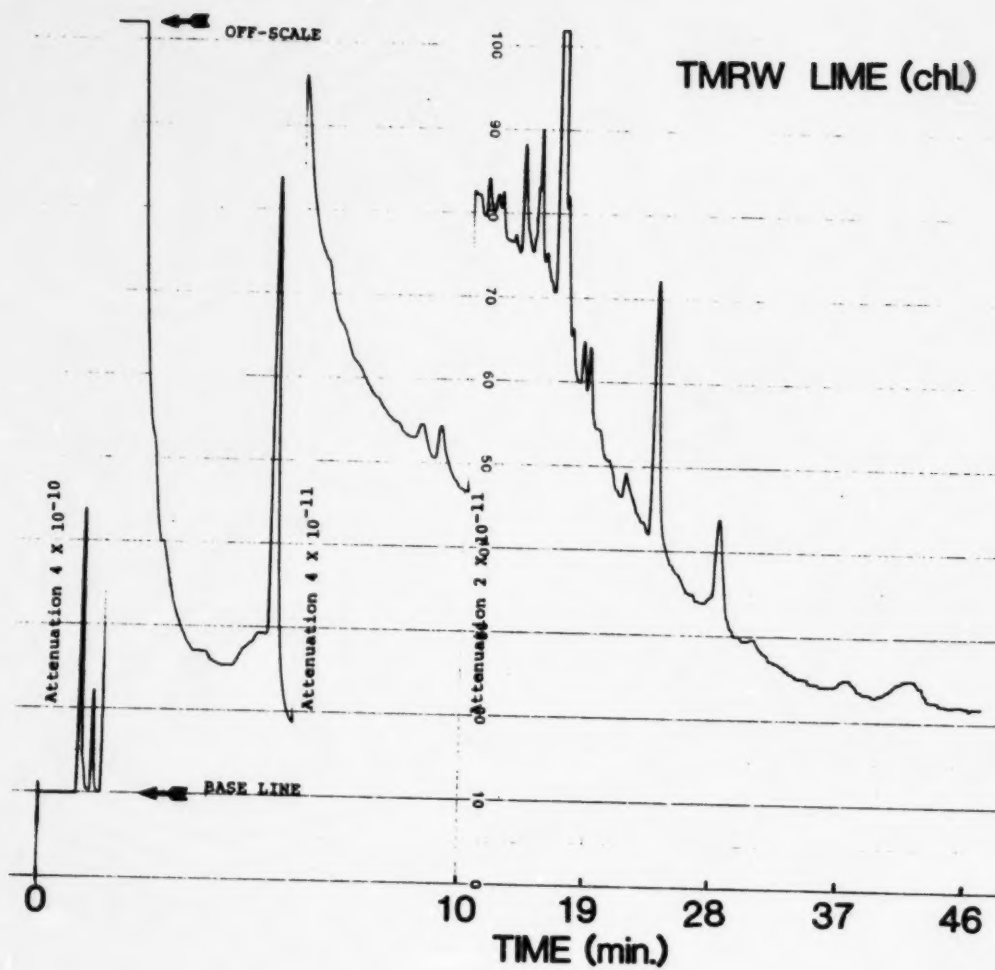


Figure 78. GC/FID analysis of chlorinated, lime treated Mississippi River water.

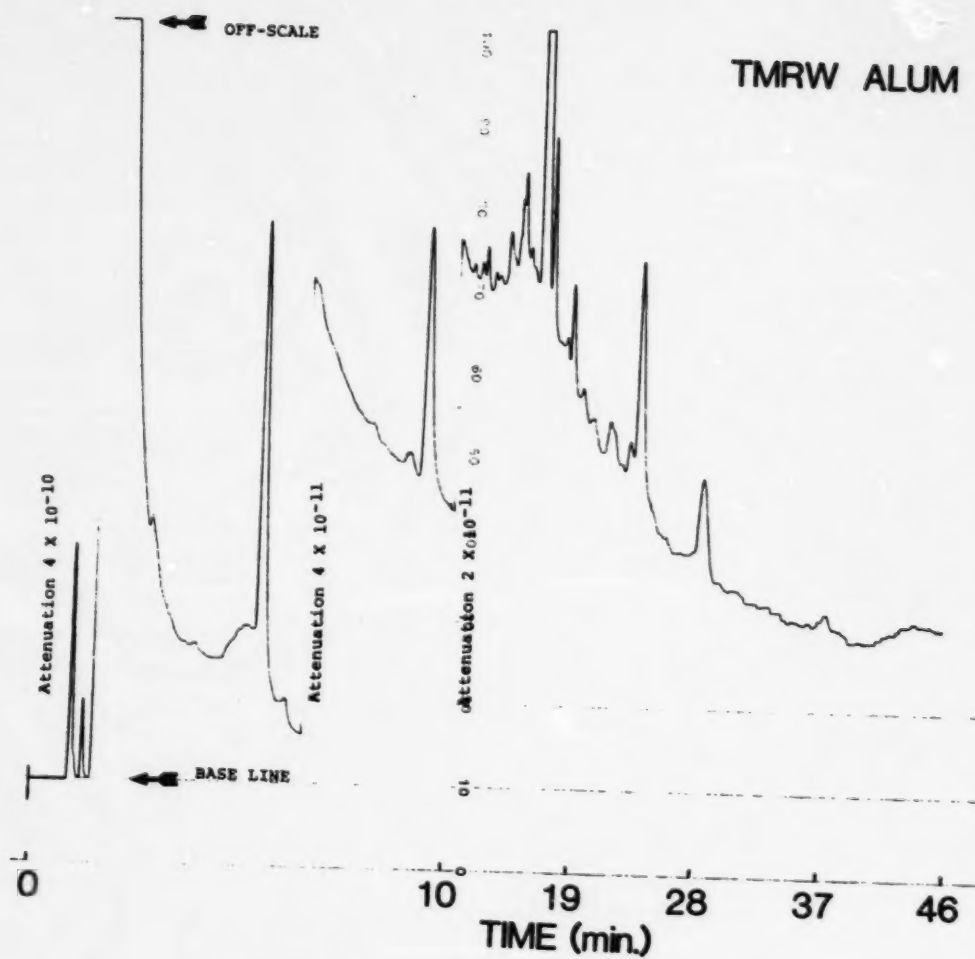


Figure 79. GC/FID analysis of alum pretreated Mississippi River water.

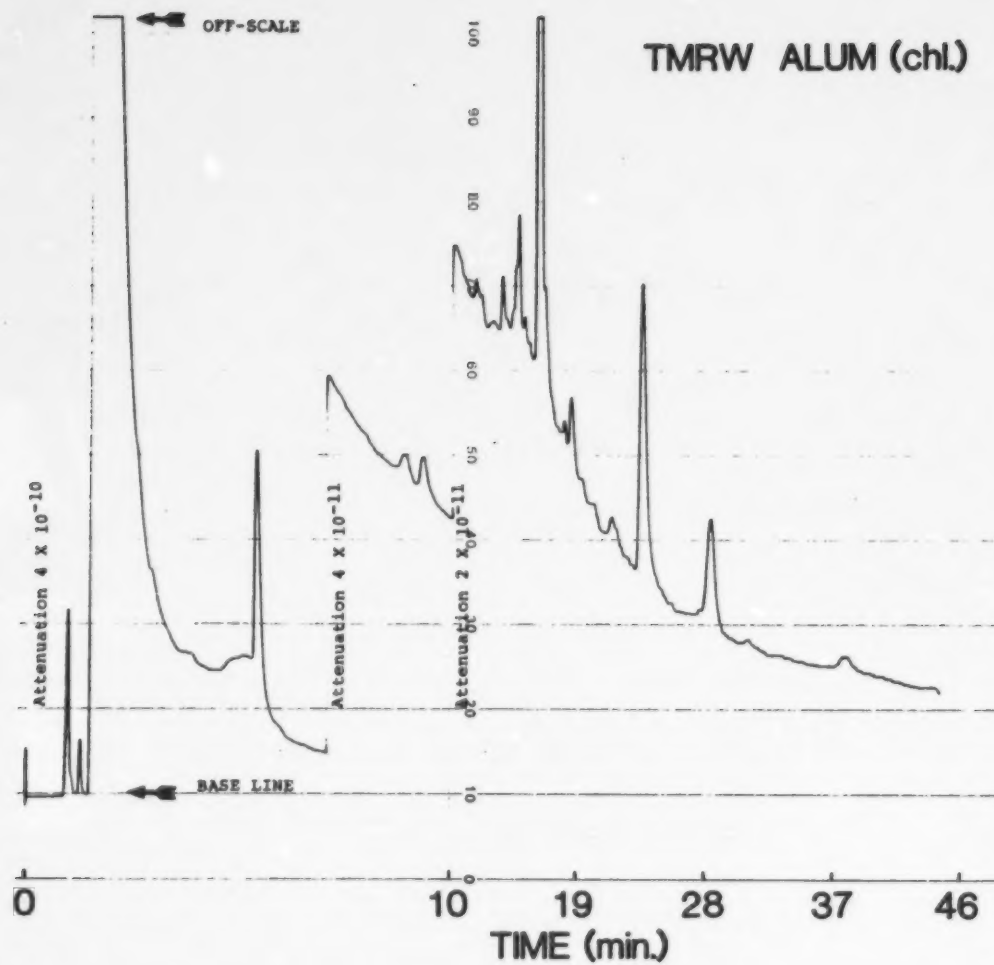


Figure 80. GC/FID analysis of chlorinated, alum pretreated river water.

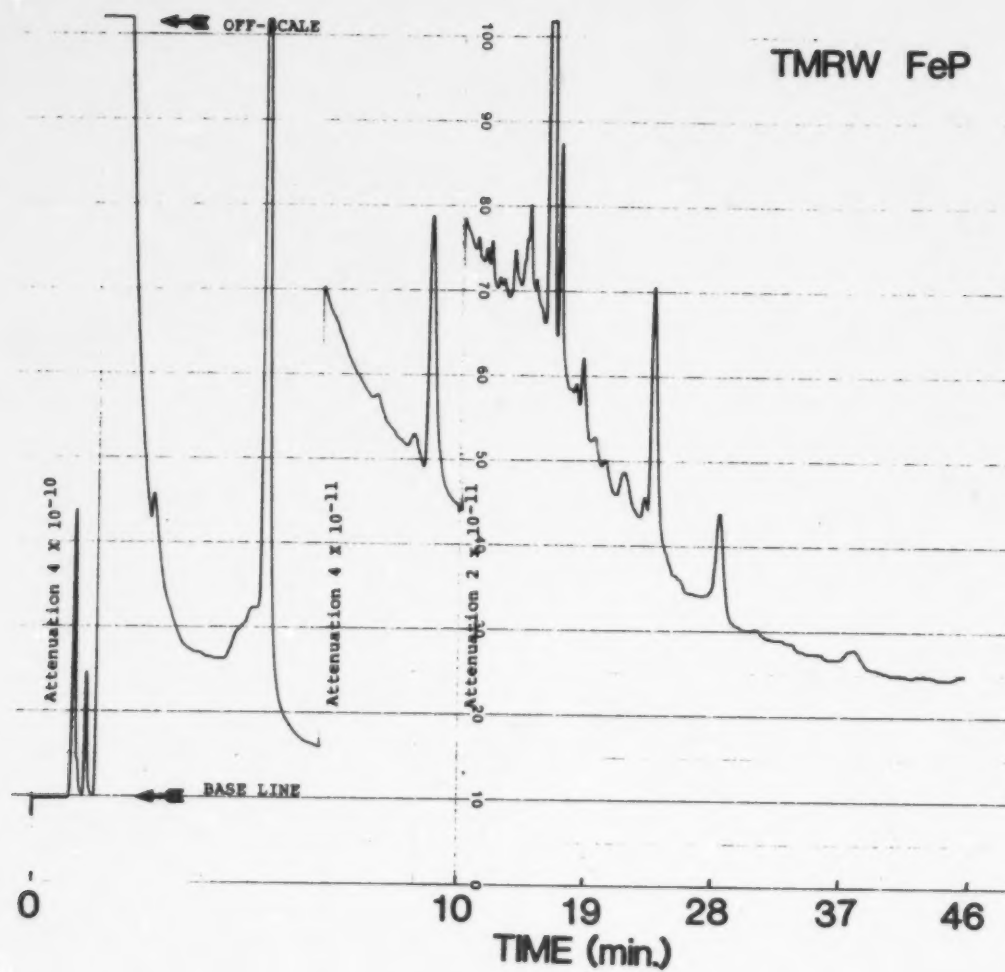


Figure 81. GC/FID analysis of iron and polymer pretreated river water.

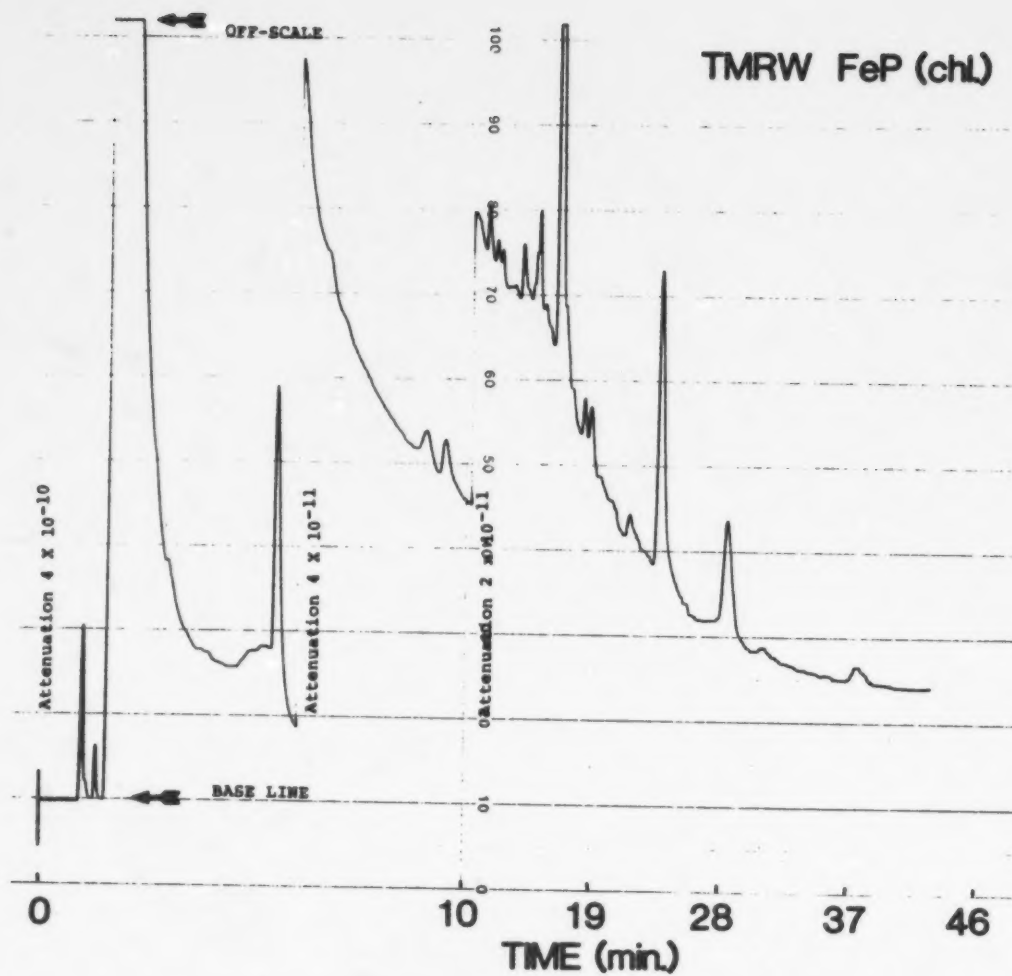


Figure 82. GC/FID analysis of chlorinated, iron and polymer pretreated river water.

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are shown in Figures 83 and 84. The results indicate that carbon does not significantly alter the organic profile after RRT = 0.9, and chlorination of the water does not alter this profile either. However, the first section of the chromatogram for the unchlorinated water (Figure 83) indicated that several peaks were present that were not observed in lime pretreated or river water samples. Three new peaks were observed at RRT's of 0.23, 0.33 and 0.36 and the peak at RRT = 5.56 and its shoulder were very much larger than that observed in the pretreated or river water samples (Figures 77 and 75, respectively). In addition, the peaks eluting earlier than the solvent peak were very much larger than those observed in the previous figures. A similar response was obtained with the alum + GAC profile shown in Figure 85. With alum pretreatment the carbon effluent yielded large pre-solvent peaks, a peak at RRT = 0.29 and a very large peak at RRT = 0.56. Other investigators (111) have noted similar changes in the GC profile following carbon treatment. This may be caused by aerobic organisms reducing the oxygen content of organic compounds to such an extent that these compounds are rendered chromatographable and detectable by FID (111).

The early eluting peaks in Figure 83 may have been caused by a mistake made during the solvent extraction of the XAD resin following its use to concentrate the organics in the lime pretreated GAC effluent. Acetone (distilled in glass, Burdick and Jackson) was inadvertently employed initially to extract the resin. When the mistake was realized, the usual procedure with ether was initiated. Milli Q water was employed to separate the acetone from the ether and the ether was reduced in volume and tested. Any acetone remaining in the ether would be eluted in the solvent peak and none of the observed peaks were attributable to the acetone. However, it is possible that the presence of acetone may account for the extra early eluting peaks.

The large peak observed at RRT = 0.56 represents a volatile organic compound that was not removed by carbon adsorption. The larger size of this peak in Figure 83 compared to Figure 77 (lime treatment only) may be explained by the relative volumes of water extracted. Interestingly, chlorination of the carbon treated water completely eliminated the compounds contributing to the peaks at RRT's of 0.23, 0.33, 0.36 and 0.56 but had no discernable effect upon the later eluting compounds. This effect was also apparent when the alum + GAC treated effluent was chlorinated as shown in Figure 86.

The carbon effluent for the iron and polymer pretreated water was also tested but the unchlorinated sample was lost. The chlorinated effluent profile was essentially identical to Figure 86, however, and no peaks were discernable until RRT's >0.8.

In summary, therefore, it appears that with the small volume of water concentrated the low molecular weight volatile compounds detected were poorly removed by any of the treatment combinations studied and similar chromatograms were obtained for all the samples tested. Chlorination was observed to form a relatively non-volatile product in the river water sample, but in pretreated water samples chlorination appeared to reduce the concentrations of some compounds (peaks). In the case of carbon treated waters early eluting peaks were detected, especially for lime pretreated water that were

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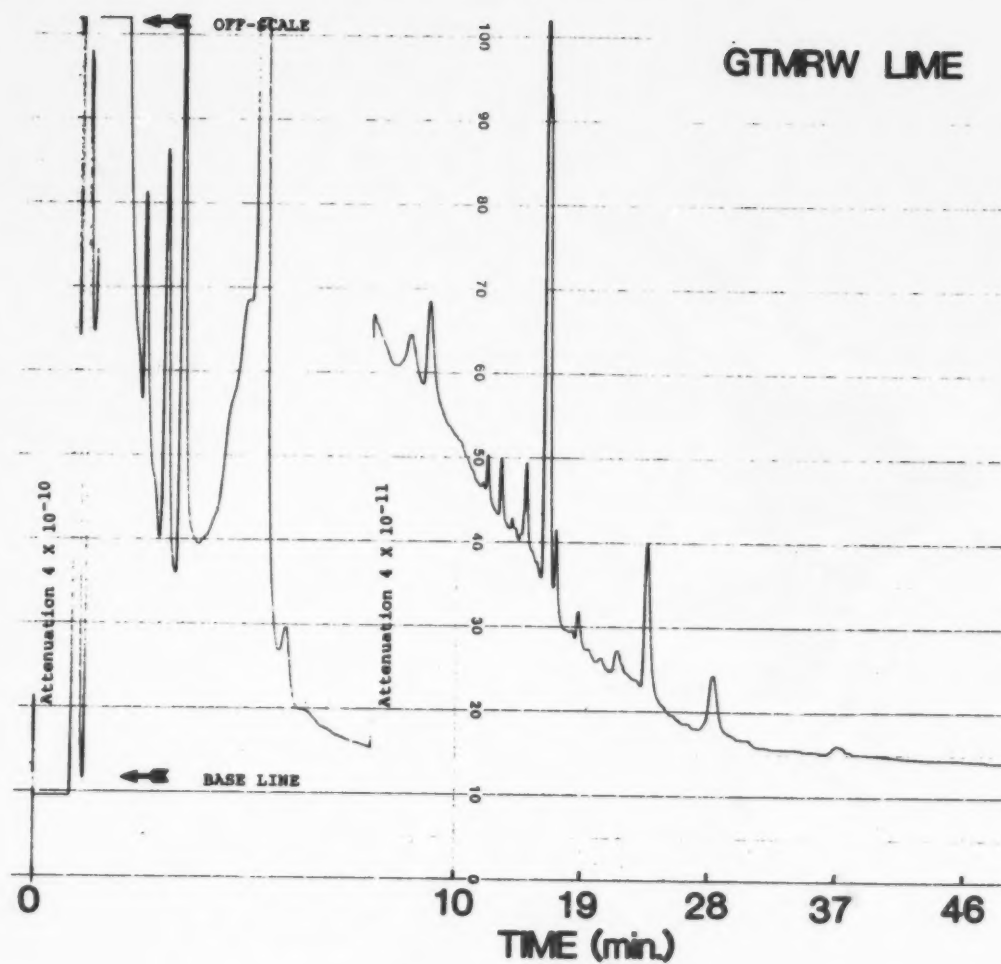


Figure 83. GC/FID analysis of water sample following lime pretreatment and GAC treatment.

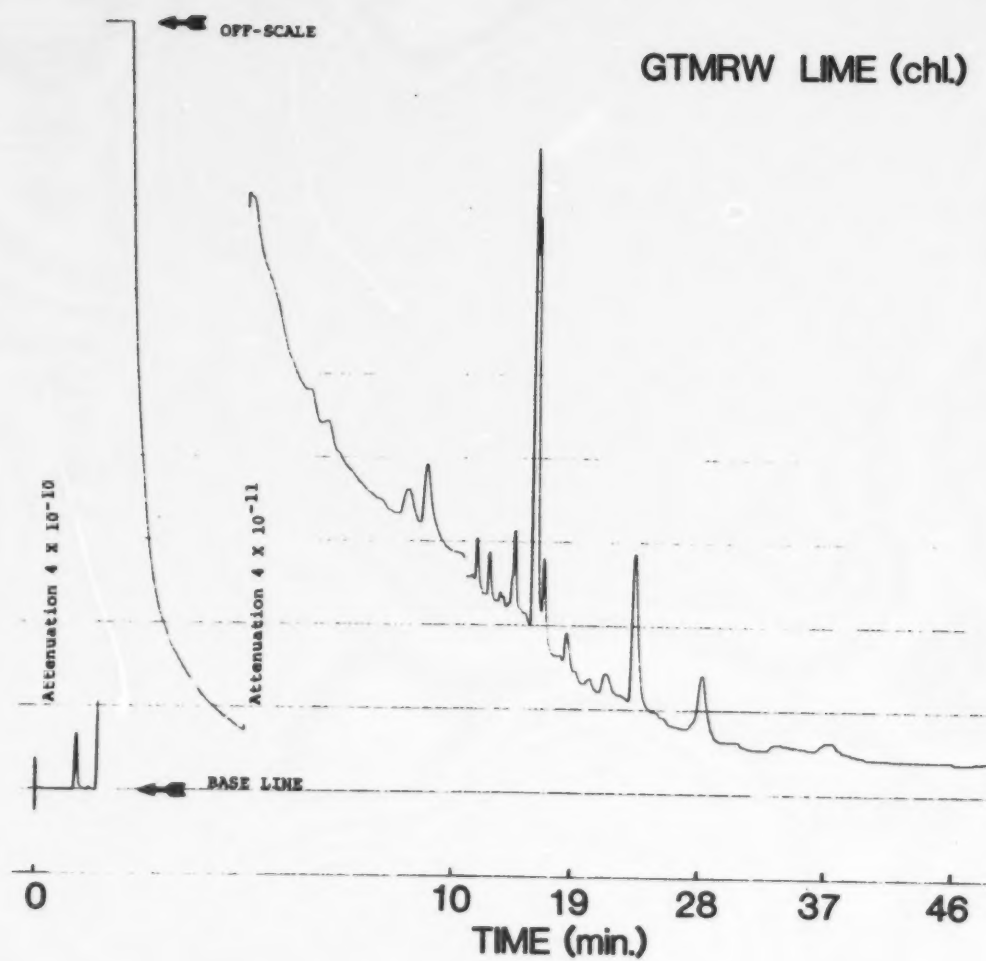


Figure 84. GC/FID analysis of water sample chlorinated after lime treatment and GAC.

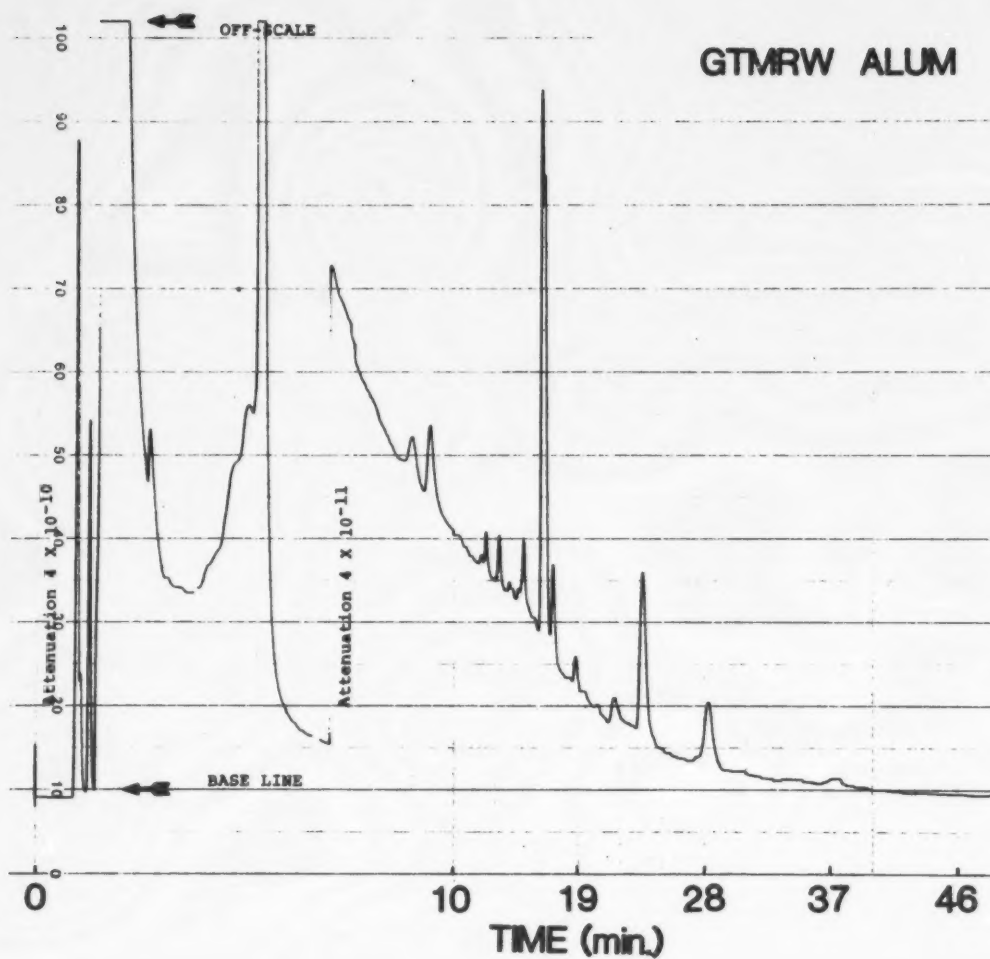


Figure 85. GC/FID analysis of water samples following alum pretreatment and GAC treatment.

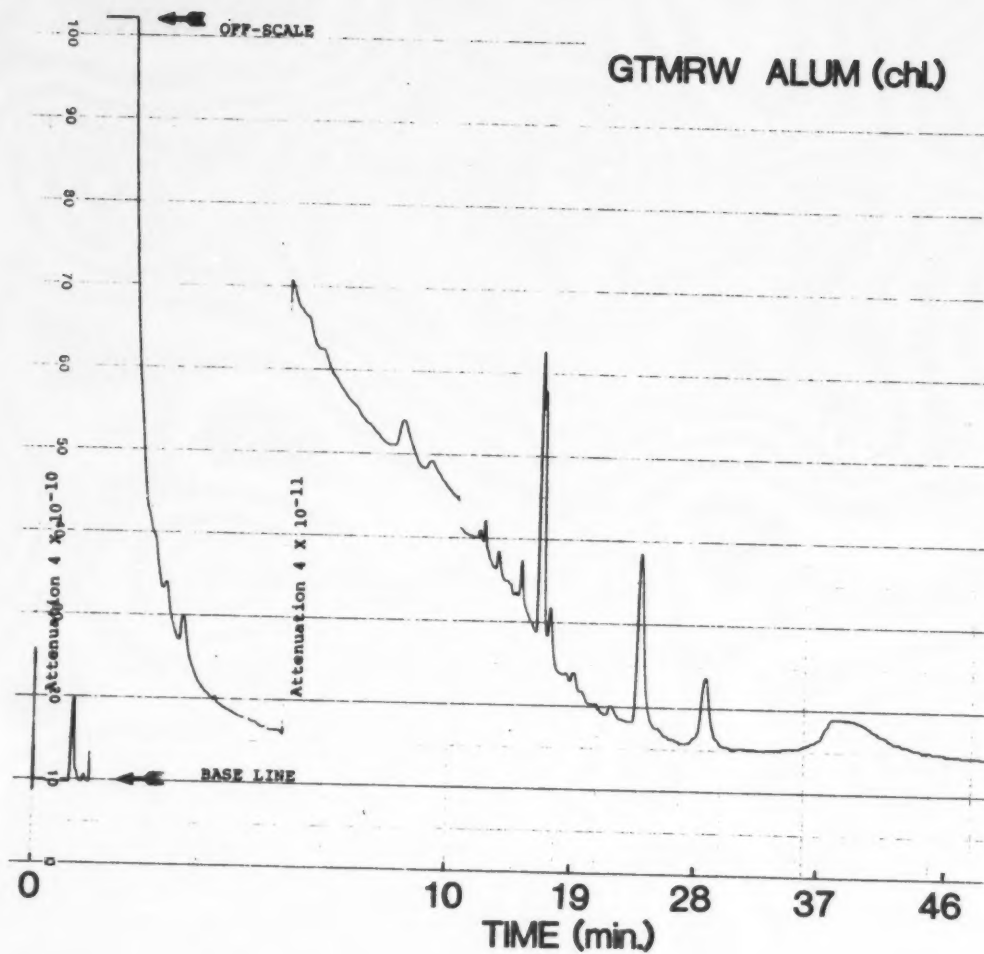


Figure 86. GC/FID analysis of water sample chlorinated after alum treatment and GAC.

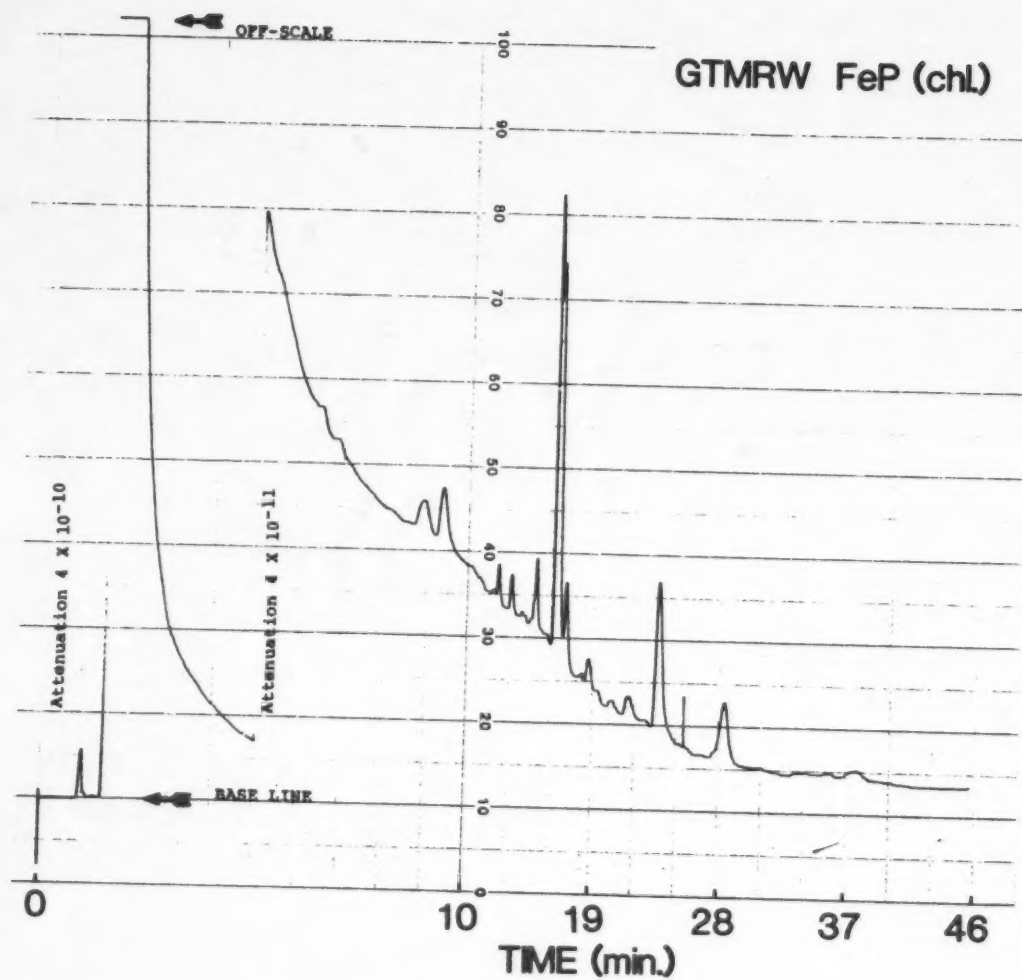


Figure 87. GC/FID analysis of a water sample chlorinated after iron and polymer pretreatment and GAC.

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not present in the pretreated or river water samples. This may have been caused by a different extraction procedure, however. Chlorination of the carbon treated waters caused the earlier eluting peaks to disappear from the GC/FID profile. In retrospect the techniques used in this portion of the study (GC/FID analyses) were not successful.

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SECTION 8

ACTIVATED CARBON COLUMN PERFORMANCE STUDIES

To investigate the impact of pretreatment on carbon adsorption an experimental design was required that would allow an evaluation of carbon performance in a reasonable time. One way of accomplishing this is to evaluate adsorption capacity by means of a batch equilibration technique. This technique has been employed by a large number of investigators and is a standard method of comparing the adsorption behavior of different systems. However, in heterogeneous multicomponent systems there is no easy way to relate the observed batch isotherm data to carbon column performance for given operating conditions. The batch studies may provide a qualitative indication of relative adsorption capacities, but their utility is limited in practical application, and pilot column studies are usually undertaken to obtain performance data. Pilot studies on activated carbon columns take many months to complete and, accordingly, they are expensive to run. In addition, because of the long time frame over which the study is conducted, water quality variations in the influent water make it difficult to identify the impact of different operating conditions on performance.

In this study, miniature carbon columns were employed to model the behavior of full-scale units and performance curves were obtained in approximately 2 weeks. The exact design of the carbon beds was an important aspect of the study. The carbon employed in the mini-columns was 50 x 80 mesh (0.297 to 0.176 mm) and was obtained by grinding and sieving a sample of Westvaco Nuchar WV-G, 12 x 40 mesh, commercial carbon. The entire sample was reduced to less than 50 mesh in diameter so that the carbon used in this study would be representative of the commercially available carbon.

The average particle diameter employed in the study was approximately 0.22 mm and a glass column with a diameter of 9 mm was used to provide a column diameter to particle diameter of approximately 40:1. This ratio is acceptable for a column study and ensured that the wall effects were negligible.

The kinetics of organics removal by activated carbon have been simply described by expressions in which the rate of adsorption assumed to be linearly related to the concentration gradient across a stagnant liquid film surrounding the carbon particles: (107)

$$\frac{dC}{dt} = k_f A_p (C - C^*) \quad (1)$$

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C = actual concentration of organics in solution mg/L

t = time (secs.)

C^* = equilibrium concentration of organics in solution in equilibrium with the carbon surface (mg/L)

A_p = external surface area of carbon particles available for mass transfer (cm^2/cm^3)

k_f = liquid film mass transfer coefficient ($\text{cm}^{-2}\text{sec}^{-1}$)

This equation may be expanded since

$$A_p = \phi \pi d^2 n \quad (2)$$

d = diameter of carbon particle (cm)

n = number of carbon particles/unit volume

ϕ = a shape factor to account for deviation from spherical particles and for surface roughness

Further, if it is assumed that the porosity of carbon is independent of particle size, then

$$n = \frac{6(1-\epsilon)}{\pi d^3} \quad (3)$$

where ϵ = porosity of carbon bed.

Substituting (3) into (2)

$$\begin{aligned} A_p &= \phi \pi d^2 \frac{6(1-\epsilon)}{\pi d^3} \\ &= \frac{6\phi(1-\epsilon)}{d} \end{aligned} \quad (4)$$

The value of the film transfer coefficient k_f is influenced strongly by the hydraulic regime that prevails in the packed bed. Because of difficulty in describing the exact conditions of flow within a carbon bed, the value of k_f may be obtained indirectly from empirical correlations of the mass transfer factor j_d (defined below) with dimensionless numbers such as Reynolds number (Re). These correlations have been developed by numerous investigators in well defined experiments and are available in the literature (108-111). For example, Pfeffer and Happel (110) showed that for porosities between 0.4 and 1.0 the relationship in equation 5 is valid for low Reynolds numbers in a packed bed.

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$$j_d = Be(Re)^{-0.67} \quad (5)$$

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where Be is a dimensionless constant:

$$Be = 1.26[1-(1-\epsilon)^{5/3}]^{1/3} \cdot [2-3(1-\epsilon)^{1/3} + (1-\epsilon)^{5/3} - 2(1-\epsilon)^2]$$

and

$$Re = \frac{d \cdot \bar{U}}{\nu}$$

$\bar{U}$ = superficial velocity of flow

ν = kinematic viscosity of the water at temperature of column operations

Under the conditions of normal carbon column operation in water treatment, $Re \approx 2$ to 6 and $\epsilon \approx 0.4$ to 0.5. The above correlation, therefore, should be applicable to the carbon columns used in this study. If it is assumed that the porosity of the carbon remains constant and independent of particle size, then Be is a constant. The value of k_f may be evaluated from equation (5) and expressed in terms of

$$j_d = \left(\frac{k_f}{\bar{U}}\right) \cdot \left(\frac{\nu}{D_L}\right)^{2/3} \quad (\text{dimensionless}) \quad (6)$$

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to obtain a simplified expression for water at constant temperature.

$$k_f = K' d^{-0.67} \bar{U}^{0.33} \quad (7)$$

Combining equations 4 and 7 into equation 1 it may be shown that

$$\frac{dC}{dt} = K'' \frac{\bar{U}^{0.33}}{d^{1.67}} (C-C^*) \quad (8)$$

This equation indicates that the kinetics of exchange are strongly dependent upon carbon particle size and to a lesser extent upon the column loading rate $\bar{U}$. As the carbon size decreases, the kinetics of organics removal increase rapidly and a smaller carbon bed depth is required for a given degree of organic removal. Equation 8 was employed in a very simplistic way to evaluate the approximate bed depth of 50 x 80 mesh carbon that would allow simulation of the behavior of a 3 foot bed of 12 x 40 mesh carbon loaded at 2 gpm/ft². It was assumed that if the "mass transfer coefficient" ($K'' \cdot \bar{U}^{0.33} d^{-1.67}$) were doubled for a given number of bed volumes of water treated, then the same level of organics removal could be achieved in half the depth or contact time. In this fashion a carbon depth of between 6 and 9 cm containing 50 x 80 mesh carbon was estimated as necessary to simulate the behavior of a 3 ft. carbon bed of commercial carbon at the same loading rate.

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This type of analysis was helpful in picking a range of flowrates and

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bed depths that were tested initially to identify operating conditions that would yield a well defined breakthrough curve that would perhaps be representative of the anticipated behavior of a large-scale adsorber.

The above analysis was conducted assuming film diffusion control; however, if particle diffusion control is assumed, a similar scale-up relationship may be evaluated. This analysis is very simplistic and it is not intended to imply that the observed behavior in mini-columns accurately reflects the full-scale behavior of GAC columns. Rather it is intended to demonstrate that the kinetics of adsorption can be speeded up and useful data can be collected in smaller mesh carbon studies.

Results:

Initially, three carbon columns were set up with bed depths of 3, 6 and 9 cm. In addition, a sand column was operated as a control. The sand column was a larger column having an internal diameter of 15 mm and contained a 9 cm deep sand bed. This column provided a large surface area for the attachment of micro-organisms and was intended to provide some indication of the contribution of biological activity to the observed reduction in total organic concentration in the carbon columns. The column performance was monitored by measuring ultraviolet absorbance of the column effluent at 2 hour intervals. The influent was pretreated with 50 mg/L of alum at pH 5.0, filtered, and the same influent was pumped to each of the test columns at 5 mL/min (1.92 gpm/ft²).

The results indicated the expected trend of improved removal with increasing carbon bed depth as shown in Figures 88, 89 and 90. The 9 cm column gave the most desirable breakthrough curve which initially removed most of the UVA, and after a well defined time the effluent organic concentration rose. With the shorter columns, breakthrough occurred too soon (or immediately for the 3 cm column) and these conditions were not desirable for making comparisons in column performance. As a result of this study, a 9 cm bed depth and loading of 5 mL/min was adopted as standard. This was later adjusted to a 6 cm bed depth and 3.5 mL/min to reduce the volume of water handled in the tests.

These early results also identified operating difficulties in the experimental procedure. Headloss built up over the test period because of the very small carbon particles in the columns. This caused a drop in flowrates towards the end of the runs and contributed to the improved organics removal after 160 hours of operation for the deepest carbon bed (Figure 90). Subsequently, the carbon columns were backwashed once every 2-3 days or as needed to prevent excessive headloss.

The organic concentration in the effluent from the sand control column showed some variation. It ranged between 110% and 70% of the feed concentration, and immediate breakthrough occurred, indicating that removal in the GAC column was primarily due to adsorption, not filtration. However, a clear trend in reduced effluent organic content was apparent with increasing time, but the reduction in organic concentration was small compared to

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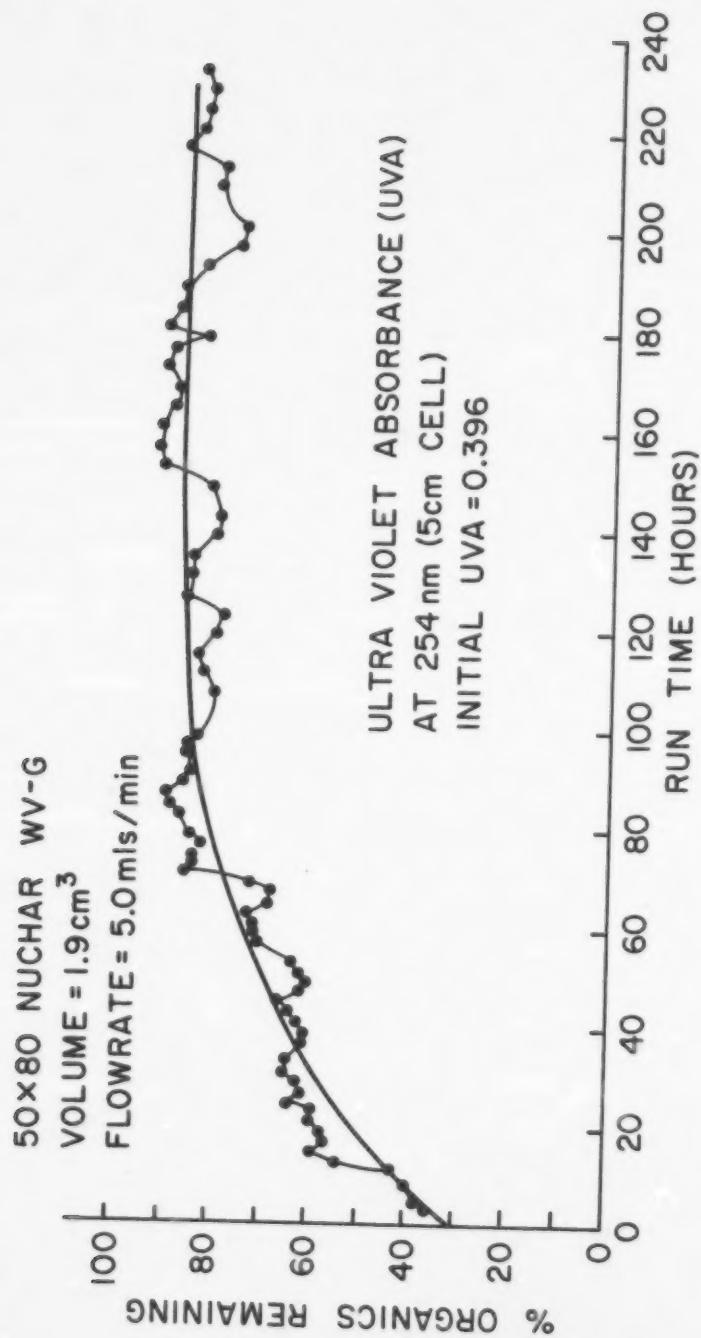


Figure 88. UVA removal from coagulated Mississippi River water in 3 cm bed of carbon.

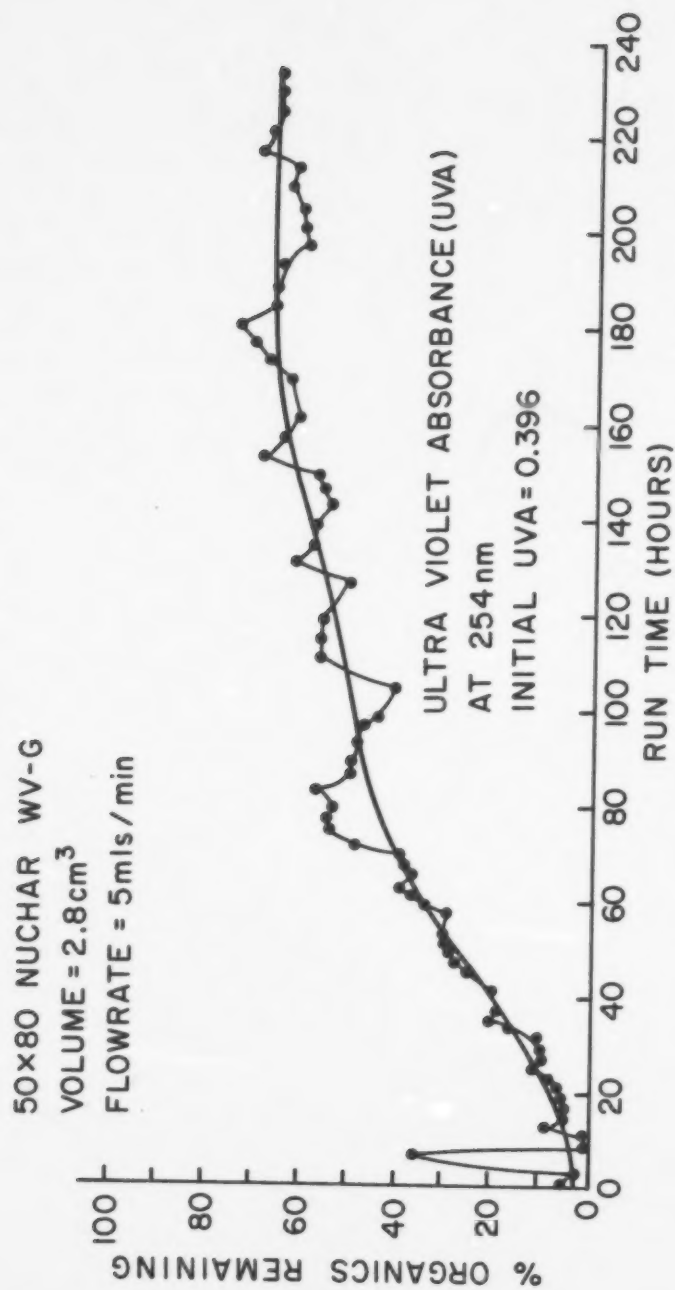


Figure 89. UVA removal from coagulated Mississippi River water.
in a 6 cm bed of carbon

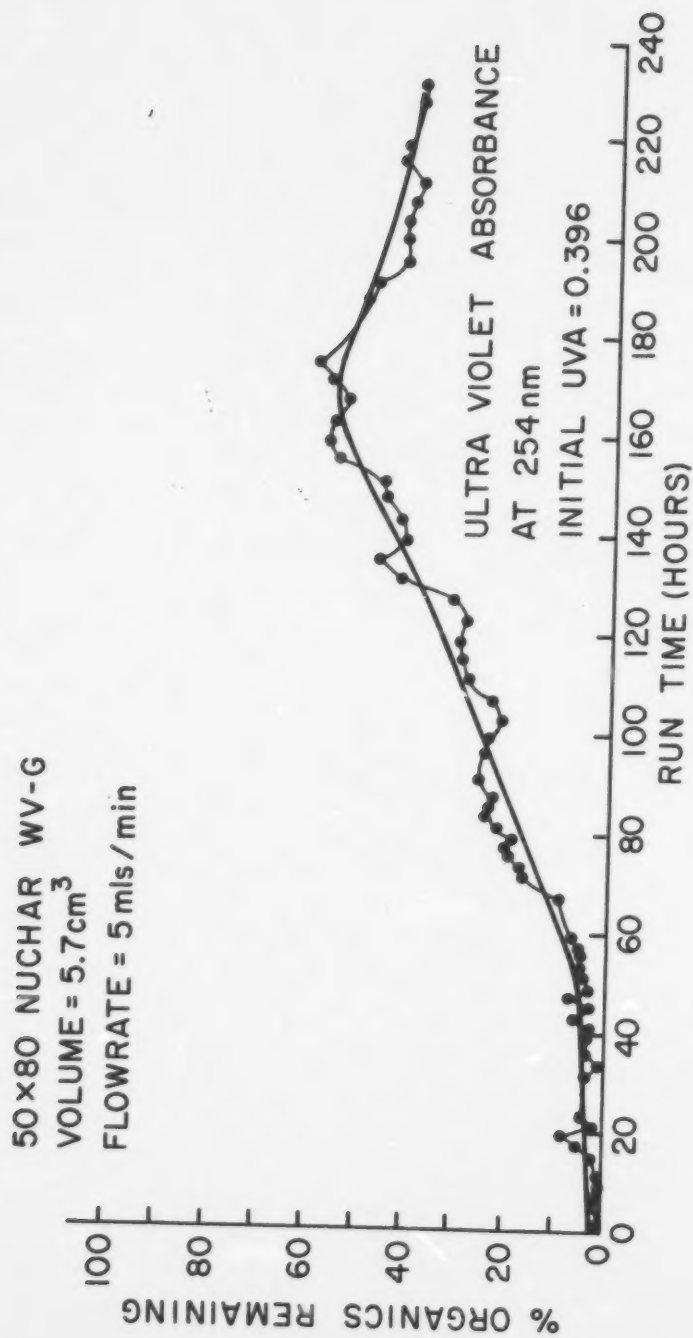


Figure 90. UVA removal from coagulated Mississippi River water in 9 cm bed of carbon.

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that observed in the carbon columns. The extent of removal by biological activity, therefore, appeared to be small relative to the observed removals by adsorption. One may, therefore, also assume that the results obtained in the carbon column studies did not include significant biological removals during the test period (~ 2 weeks).

Influence of Solution pH

The impact of solution pH upon carbon column performance was evaluated for pretreated river water. Pretreatment consisted of coagulation with 100 mg/L of alum at pH 5.0 and the settled water was prefiltered through a tri-media filter as described in Section 3.

The pH of the filtrate was then adjusted to different levels for each carbon column using NaOH or H₂SO₄. Three carbon columns were operated at pH values of 4.9, 7.0 and 8.7, respectively. A fourth column containing sand was employed as a control. The sand column measured 1.5 cm in internal diameter and contained a 10 cm depth of sand. The empty bed contact time in the control column was approximately 5 minutes.

The results of the first test are reported in Figures 91 and 92. The breakthrough in ultraviolet absorbance for the three carbon columns is presented in Figure 91. The curves clearly suggest that operation at low pH improves the organic concentrations observed and the breakthrough curves rose much less rapidly when the lower pH values were used for adsorption. The very shallow breakthrough curves gave rise to large increases in breakthrough capacities for a desired level of organics removal as pH was decreased.

The effluent from the control column containing sand showed a 17% decline in TOC from the feed concentration of 3 mg/L. The effluent TOC from the carbon column operated at pH 8.7 reached the same level as the control column after 200 hours of operation. This suggests essentially complete breakthrough had been accomplished.

The ultraviolet absorbance data in Figure 91 may be compared with the TOC removal data presented in Figure 92. The TOC curves showed the same effect and compare favorably with the UVA removal data although the magnitude of the removals was different, depending upon the way in which the organic concentrations were measured. If one considers that the initial breakthrough TOC was 0.5 mg/L and evaluates the run time after which the effluent TOC rose by 0.5 mg/L to the 1 mg/L level, some interesting comparisons may be made. Drawing a horizontal line across Figure 92 at the 1 mg/L TOC level provides the breakthrough times shown in Table 15.

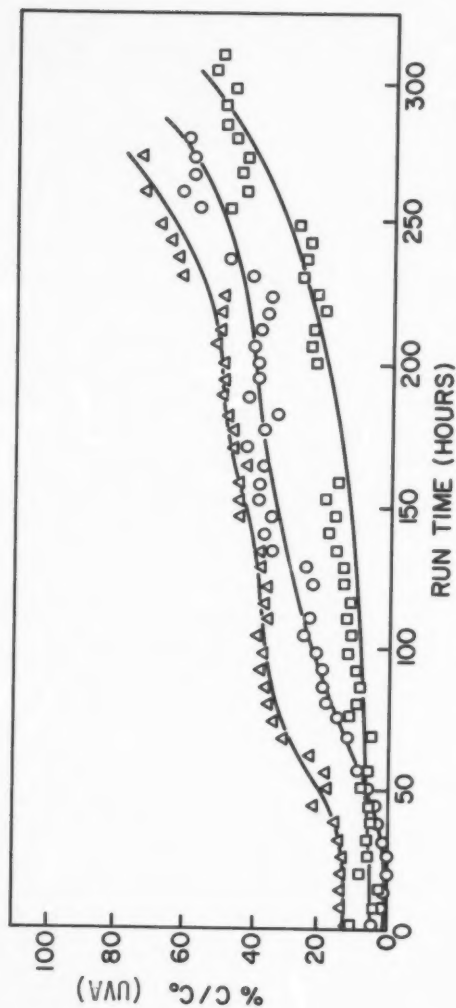
Run times may also be evaluated from Figure 92 since in this test it was noted that the ultraviolet absorbance was equal to 0.065 for an effluent TOC of 1 mg/L. Using this value for effluent UVA gave the breakthrough times also reported in Table 15.

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It is clear from Table 15 that the operating pH of the adsorption process is an extremely influential variable. The data suggests that operating capac-

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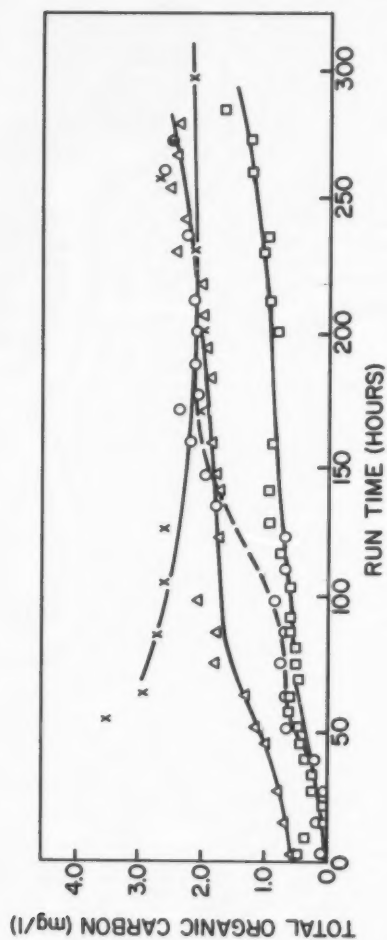


EXPERIMENTAL CONDITIONS:

- 1.) FLOWRATE = 5.0 ml/min
- 2.) COAGULATION pH = 5.0
- 3.) ALUM DOSE = 100 mg/l
- 4.) PATH LENGTH = 50 mm
- 5.) WAVELENGTH = 254 nm

COLUMN 1 - □, pH = 4.9
 COLUMN 2 - ○, pH = 7.0
 COLUMN 3 - △, pH = 8.7
 AVERAGE FEED UVA = 0.28

Figure 91. The influence of adsorption pH on % removal of UVA by activated carbon on Mississippi River water.



INITIAL FEED IS 3.0 ppm

EXPERIMENTAL CONDITIONS:

- 1) FLOWRATE = 5.0 ml/min
- 2) COAGULATION pH = 5.0
- 3) COAGULATION DOSE = 100 mg/l
- 4) CARBON TYPE-NUCHAR, 50 x 80 MESH
- 5) COLUMN DIAMETER = 0.9 cm
- 6) CARBON DEPTH = 9.0 cm

FEED TOC = 3.0 mg/l

SAND

CONTROL-

Figure 92. The influence of adsorption pH on % removals of TOC by activated carbon treating coagulated Mississippi River water.

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TABLE 15. THE INFLUENCE OF ADSORPTION pH ON THE RUN TIME FOR THE BREAK-THROUGH OF 1 mg/L TOC

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Adsorption pH	Run Time Evaluated from Figure 93 (hrs)	Run Time Evaluated from Figure 92 (hrs)
8.7	47	46
7.0	106	96
5.0	215	225

ities for an effluent TOC of 1 mg/L may be increased by a factor of 400 to 500% by reducing the pH of adsorption from 8.7 to 5.0. To verify the behavior observed in Figures 91 and 92 another test was conducted in which the adsorption pH was varied from 5.0 to 8.7. This test was conducted with Mississippi River water that had been treated with 100 mg/L of alum at pH 5.0. The empty bed contact time was 1.15 min and as may be seen in Figure 93, the results were very similar to those presented in Figure 92.

Operating at the lower pH conditions may impose troublesome constraints on construction materials to avoid corrosion problems but the long-term reduction in operating costs may outweigh the higher initial capital costs. The analysis will, however, be influenced strongly by the desired treatment objective.

For example, if an effluent concentration of 2 mg/L could be tolerated, the operating capacity may be increased by approximately 100% if the pH is reduced from 8.7 to 5.0.

The removal of trihalomethane precursors by the carbon columns was also evaluated in the duplicate test. Effluent samples from the carbon columns were chlorinated following the procedure described in Section 2 above. THM formation potentials (THMFP) were then plotted as a function of run time for the different carbon columns. The results for the study on the influence of pH are plotted in Figure 94.

The total trihalomethane formation potentials (TTHMFP) of the column effluents are shown in Figure 94 and the results indicated that THM precursor removal showed the same removal trend observed for TOC removal (Figure 93). Examination of the formation of brominated trihalomethanes in the carbon column effluents indicated that dibromochloromethane formation was not influenced significantly and varied between 0.3 and 1.2 ug/L. Bromodichloromethane formation was observed to increase with run time and higher effluent formation potentials were observed as the feed solution pH was increased from 5.0 to 8.7. Measured bromoform concentrations in the column effluents were negligible in all cases and chloroform accounted for the majority of the trihalomethanes formed in the chlorinated effluent samples.

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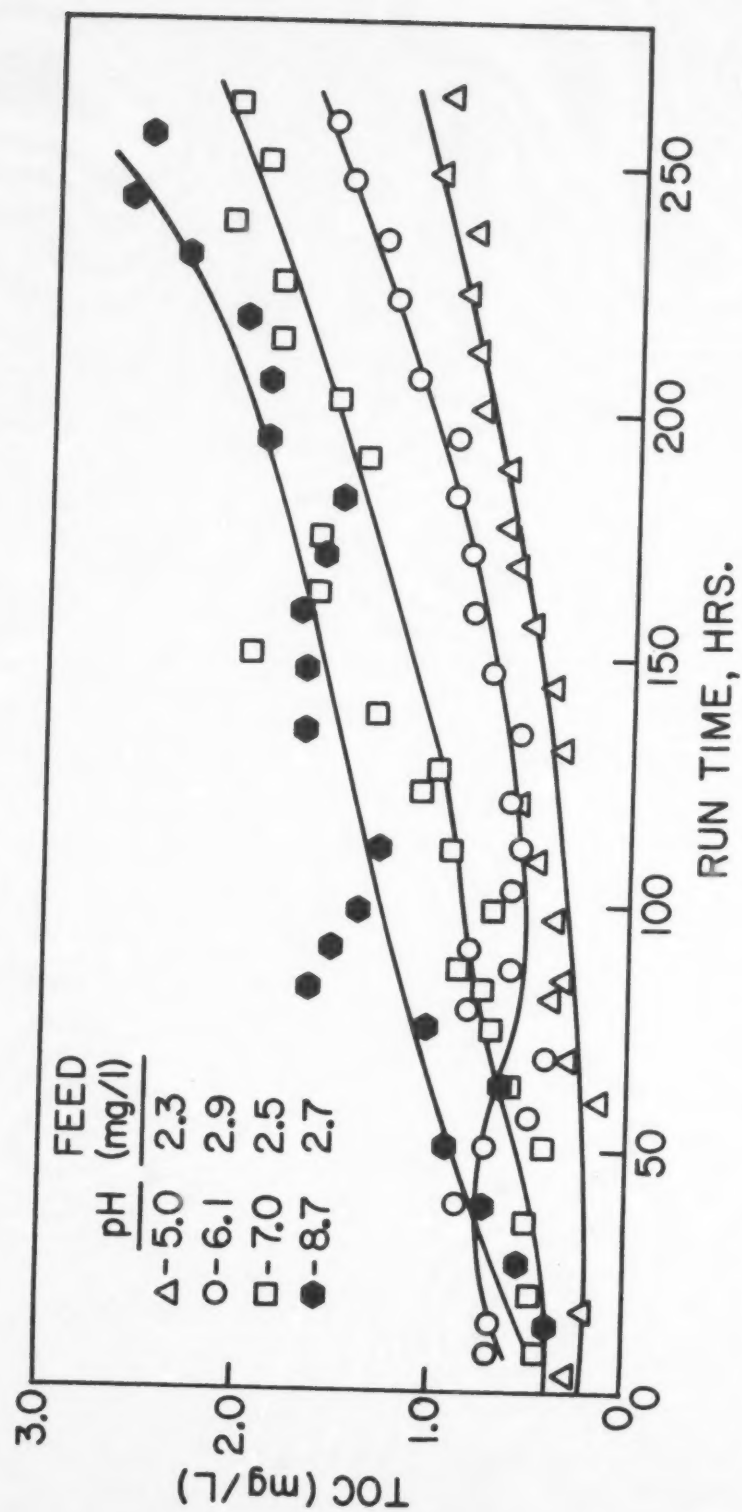


Figure 93. Run A - effect of adsorption pH on TOC removal by activated carbon.
River water coagulated with 100 mg/L of alum at pH 5.0. EBCT = 1.15 mins.

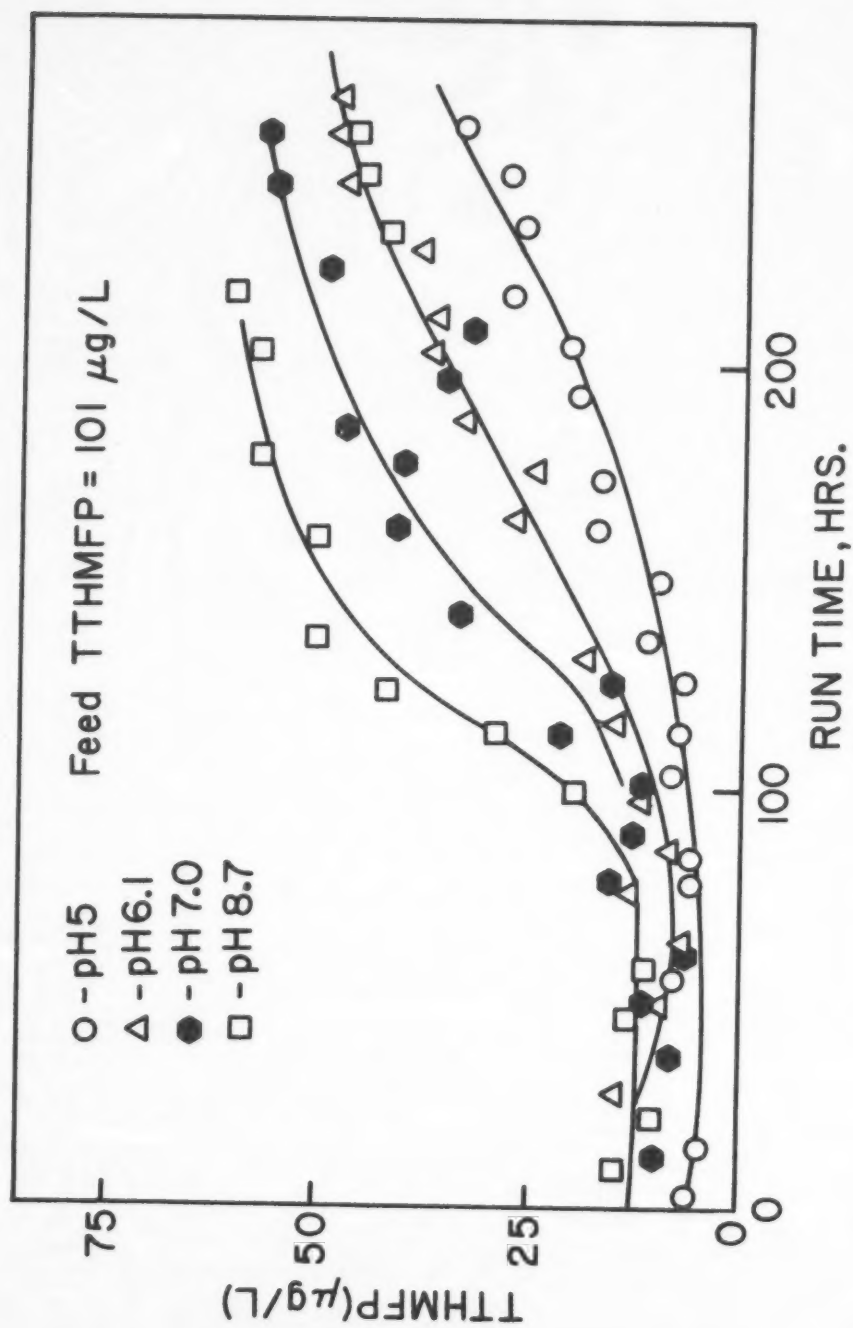


Figure 94. Run A - effect of adsorption pH on THM precursor removal from coagulated river water by activated carbon. Coagulation conditions = 100 mg/L, pH 5.0. EBCT = 1.15 mins. Flowrate = 3.5 mL/min.

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The Influence of Pretreatment on Carbon Performance

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1) Alum Coagulation:

The influence of alum pretreatment upon organics removal by activated carbon was evaluated by coagulating a river water sample with 50, 100 and 200 mg/L of alum. Coagulation was accomplished at pH 5.0 but after sedimentation and filtration, the water samples were adjusted to pH 7.0 for adsorption. Three columns were operated for the pretreated water samples and fourth column received unpretreated river water at pH 7.0 as a control to evaluate the effectiveness of coagulation pretreatment.

The breakthrough in UVA is shown in Figure 95 for the pretreated columns. The data indicate that removal of organics was improved by the use of coagulation. Without pretreatment, the organics broke through the activated carbon rapidly and low effluent UVA values could not be achieved. As coagulant dose increased, improved removal performance was observed by activated carbon and although the actual organic content of the water was decreased as the level of pretreatment was increased, the percentage removals of organics improved with increasing pretreatment. The shapes of the breakthrough curves in Figure 95 are quite similar and the curves were displaced to the right as the level of pretreatment increased. Figures 96 and 97 show the same trend in the data for TOC removal. The greater levels of pretreatment gave improved removal performance for the activated carbon. The results show the merit to improving organics removal by coagulation pretreatment, but the difference in performance between the different levels of coagulant dose was not as exaggerated as had been anticipated. The coagulant doses were based upon organics removal levels expected from earlier jar tests on the river water, but, as shown in Figures 95 and 96, the pretreated waters were not very different in organic content and the levels of pretreatment were quite similar.

All pretreatments had a profound impact on the performance of carbon. When untreated Mississippi River water was applied to a carbon minicolumn, under the same conditions as the pretreated water sample, the breakthrough curve shown in Figure 97 was obtained. It was apparent that a very poor effluent water quality resulted and low TOC levels could not be achieved without pretreatment.

Several additional studies were completed in which jar tests were conducted on the river water samples in order to identify the dose-response of the water prior to the start of a carbon column study. Figures 98 to 100 show the results of a second study (Run B) on the impact of alum dose ranging between 25 and 100 mg/L of alum. Mississippi River water was coagulated at pH 5.0 with varying alum dosages and the adsorption study was also conducted at pH 5.0. Six cm carbon beds were loaded at 3.5 mL/min to provide empty bed contact times of 1.15 minutes. The results indicated that a significant improvement in performance was achieved by increasing the alum dose from 25 to 50 mg/L but little additional benefit was observed for higher coagulant doses.

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The test results for UVA, TOC and THMFP removal showed the same general

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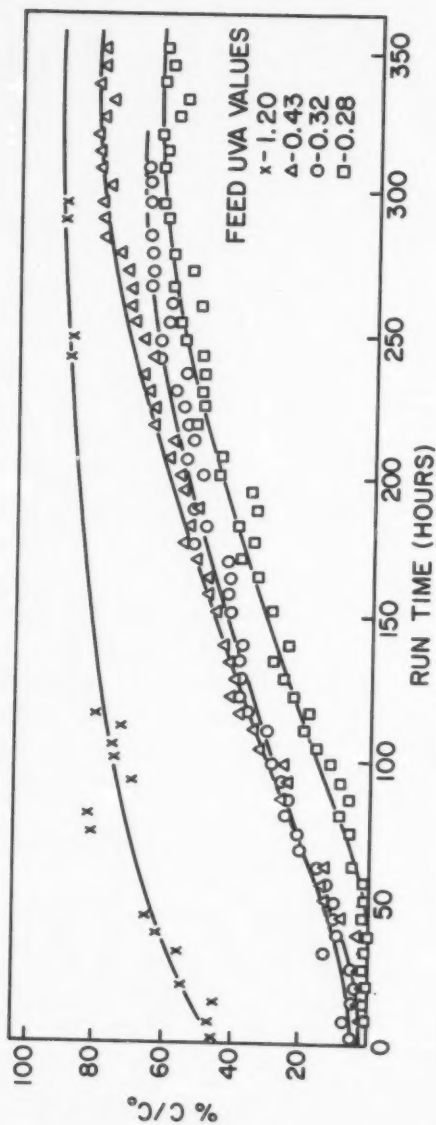
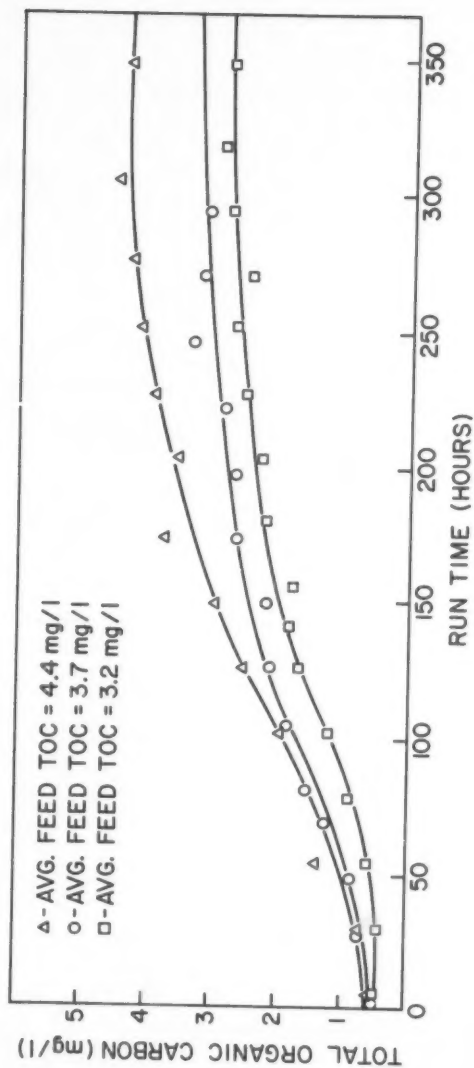


Figure 95. The influence of alum dose on % removal of UVA by activated carbon for Mississippi River water.

EXPERIMENTAL CONDITIONS:

- 1.) FLOWRATE = 3.5 ml/min
- 2.) COAGULATION pH = 5.0
- 3.) ADSORPTION pH = 7.0
- 4.) CARBON TYPE - NUCHAR WVG, 50 x 80 MESH
- 5.) EBCT = 1.15 mins.

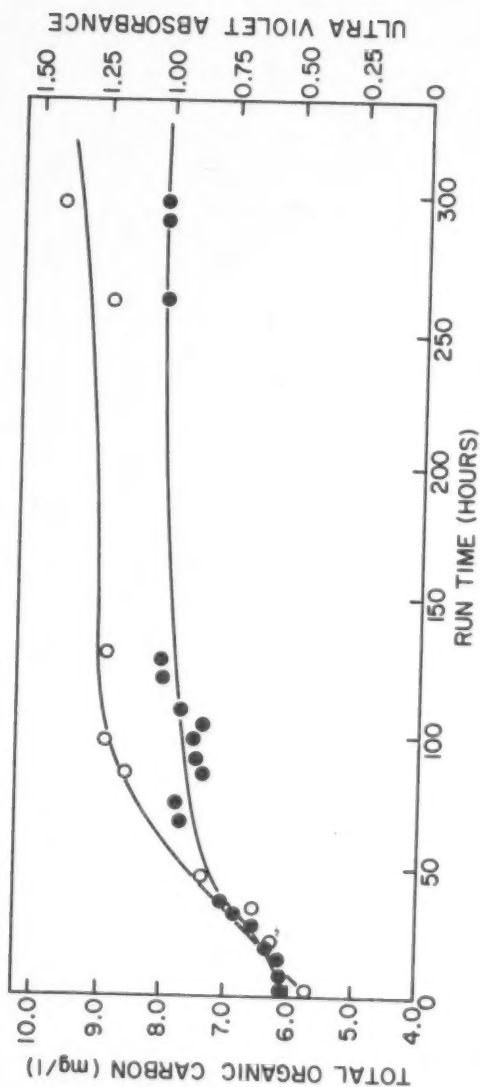
COLUMN 1 - Δ, ALUM DOSE = 50 mg/l
 COLUMN 2 - o, ALUM DOSE = 100 mg/l
 COLUMN 3 - □, ALUM DOSE = 200 mg/l
 COLUMN 4 - x, UNTREATED MRW



COLUMN 1 - Δ, ALUM DOSE = 50 mg/l
 COLUMN 2 - ○, ALUM DOSE = 100 mg/l
 COLUMN 3 - □, ALUM DOSE = 200 mg/l
 COLUMN 4 - x, UNTREATED MRW

EXPERIMENTAL CONDITIONS:
 1.) FLOWRATE = 3.5 ml/min
 2.) COAGULATION pH = 5.0
 3.) ADSORPTION pH = 7.0
 4.) CARBON TYPE - NUCHAR WVG,
 50 x 80 MESH

Figure 96. The influence of alum dose pretreatment on TOC breakthrough from activated carbon on Mississippi River water.



O - UNTREATED M.R.W.-TOC
 ● - UNTREATED M.R.W.-UVA
 INITIAL TOC FEED = 10.7 mg/l
 INITIAL UVA FEED = 1.20

EXPERIMENTAL CONDITIONS:
 1.) FLOWRATE = 3.5 ml/min
 2.) ADSORPTION pH = 7.0
 3.) CARBON TYPE - NUCHAR WVG,
 50 x 80
 4.) PATH LENGTH = 50 mm
 5.) WAVELENGTH = 254 nm

Figure 97. TOC and UVA breakthrough from activated carbon for untreated Mississippi River water.

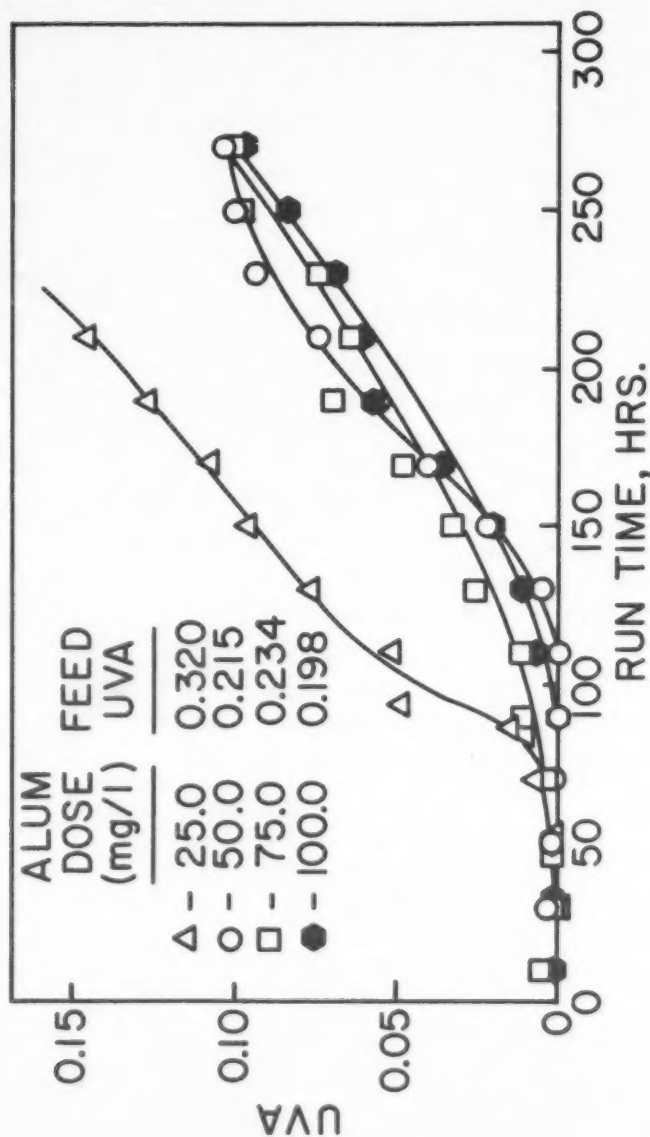


Figure 98. Run B - effect of alum dose in pretreatment on UVA removal by activated carbon at constant adsorption pH = 5.0 Coagulation pH = 5.0; EBCT = 1.15 minutes, Flowrate = 3.5 mL/min.

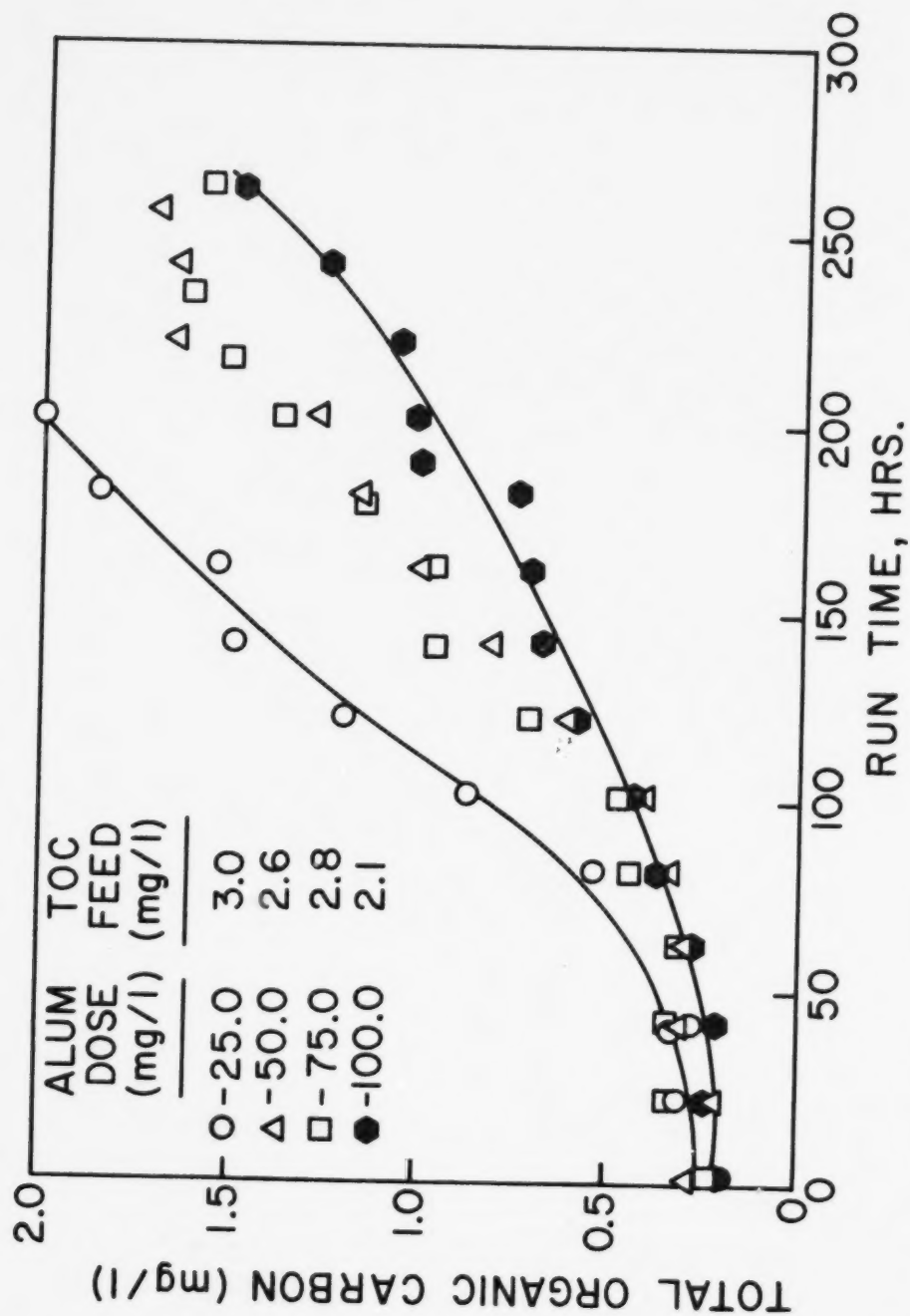


Figure 99. Run B - effect of alum dose in pretreatment on TOC removal by activated carbon at constant adsorption pH = 5.0. Coagulation pH = 5.0; EBCT = 1.15 minutes; flowrate = 3.5 mL/min.

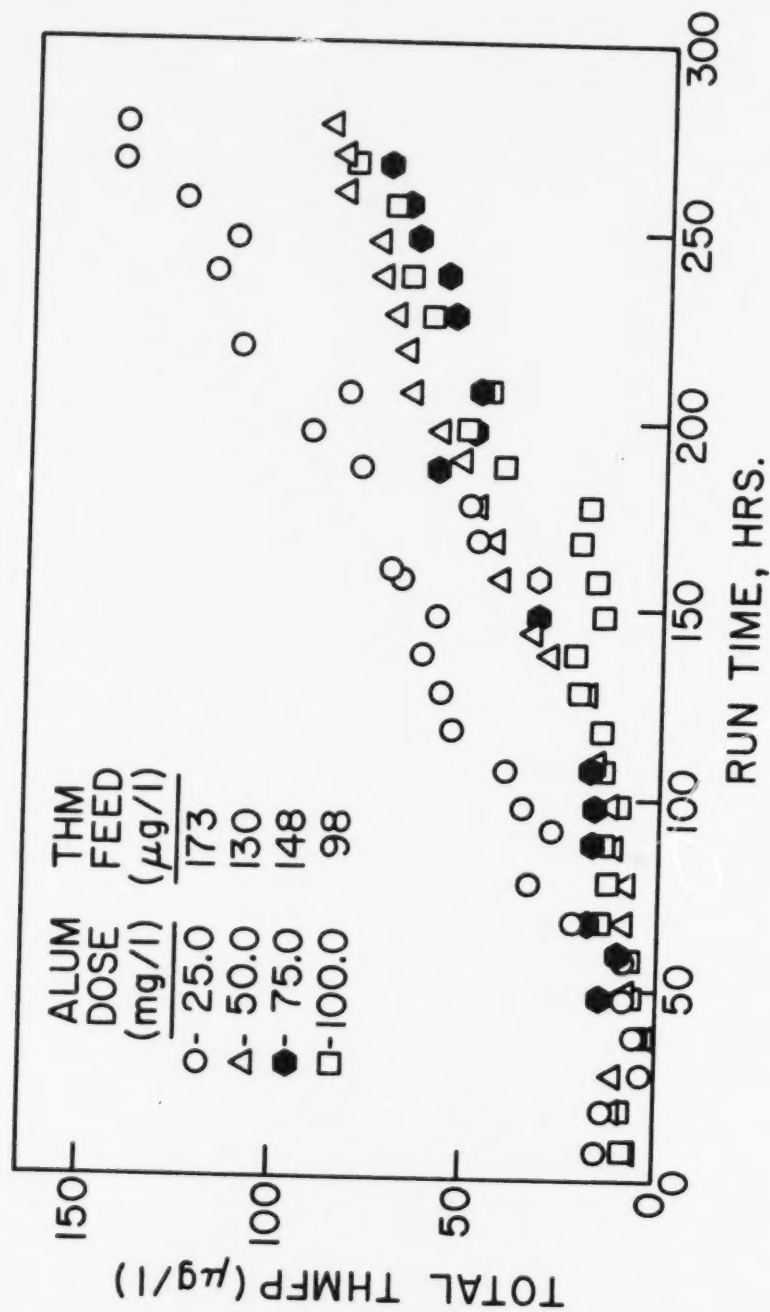


Figure 100. Run B - the effect of alum dose in pretreatment on THM precursor removal by activated carbon at constant adsorption pH = 5.0. Coagulation pH = 5.0; EBCT = 1.5 minutes; flowrate = 3.5 mL/minute.

trends regardless of the analytical technique employed for monitoring column performance.

Analysis of the effectiveness of pretreatment shows that the 50 mg/L and the 75 mg/L alum dose yielded water having very similar quality but some improvement was noted for the 100 mg/L alum dose. This trend was reflected in the carbon column performance; as the feed organic concentration was reduced, the life of the carbon was extended.

A third study (Run C) also examined the impact of alum on a freshly collected river water sample. The results are shown in Figures 101 to 104. In this study the coagulant doses gave a good range in influent water quality and the impact of alum dose was well defined. The results of the jar tests conducted at pH 5.0 on this water sample are plotted in Figure 101 and doses of 25, 50 and 75 mg/L alum were selected for pretreatment. Carbon adsorption studies were then conducted at a constant pH of 5.0. The flowrate of 35 mL/min fixed the empty bed contact time at 1.15 minutes. The trend observed in the previous studies was repeated and improved carbon column performance was observed with greater levels of pretreatment.

These results on the impact of alum dose upon carbon performance generally indicated that as the influent TOC was reduced, the carbon columns were able to treat a greater volume of water before an undesirable organic concentration broke through. To illustrate the relationship between service life and influent water quality for a constant pH, the time required for the effluent TOC to rise to 1 mg/L was plotted as a function of influent TOC, as shown in Figure 105. Plotted in this way, the data show a very strong correlation and the breakthrough time may be estimated for a given influent water quality from such a curve. It should be noted that Figure 105 is specific for the operating conditions tested, adsorption at pH 5.0 and the water samples employed in this study.

DISCUSSION

Influence of pH

Several investigators (15,70,71) have observed that the ionic form of carboxylic acids are more poorly adsorbed than the undissociated acid molecules. This difference may stem from the increased solubility of the ionized species or it may be explained in terms of the mechanism of adsorption. The surface of activated carbon is negatively charged in the neutral pH range as a result of the dissociation of surface carboxylic groups. A reduction in pH may be expected to improve adsorption since the protonation of carboxylic functional groups on both the organic acids in solution and on the carbon surface would reduce electrostatic repulsion forces, thus promoting a greater degree of adsorption.

Since the pK_a of carboxylic functional groups on natural organic matter may range between 2 and 5, the pH effect on the ionization of the organic acids should not become significant until the pH drops below pH 6.0. However, the carbon surface apparently changes in character as the pH is altered

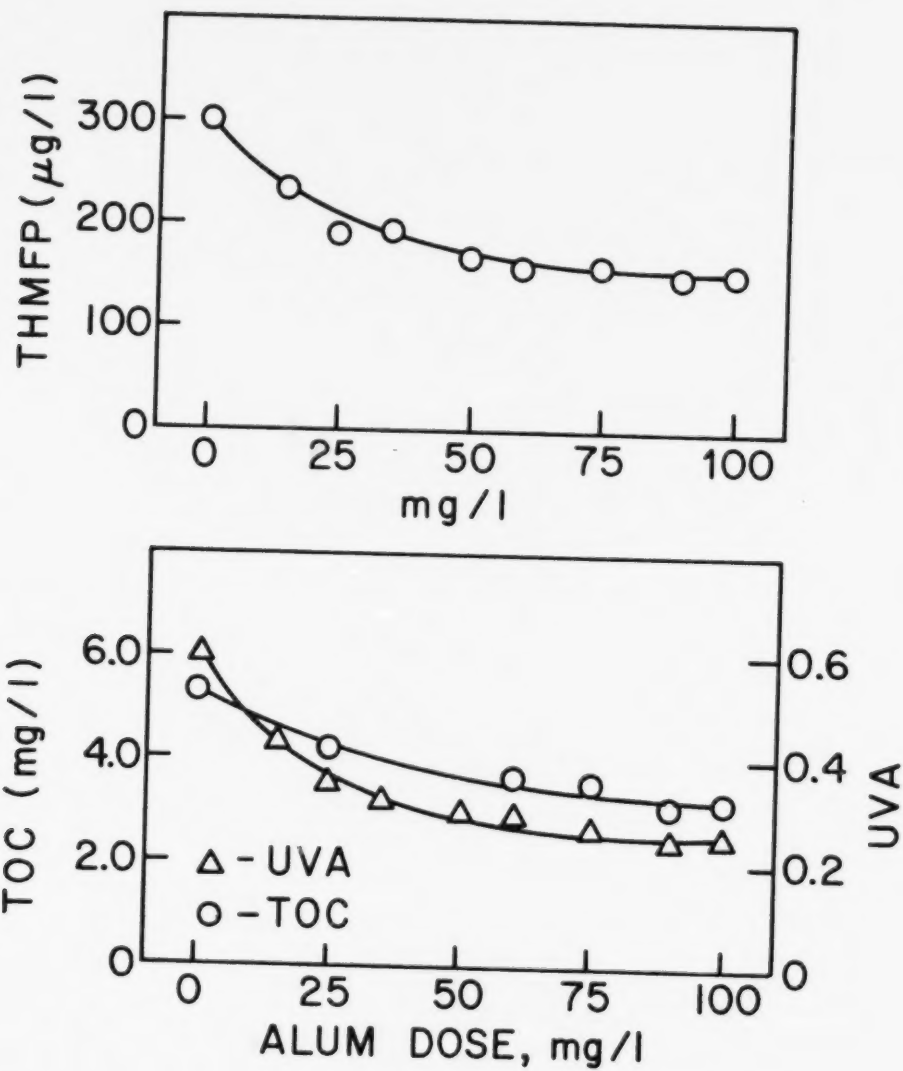


Figure 101. Jar test results - impact of alum dose on Run C feed.
Coagulation pH = 5.0.

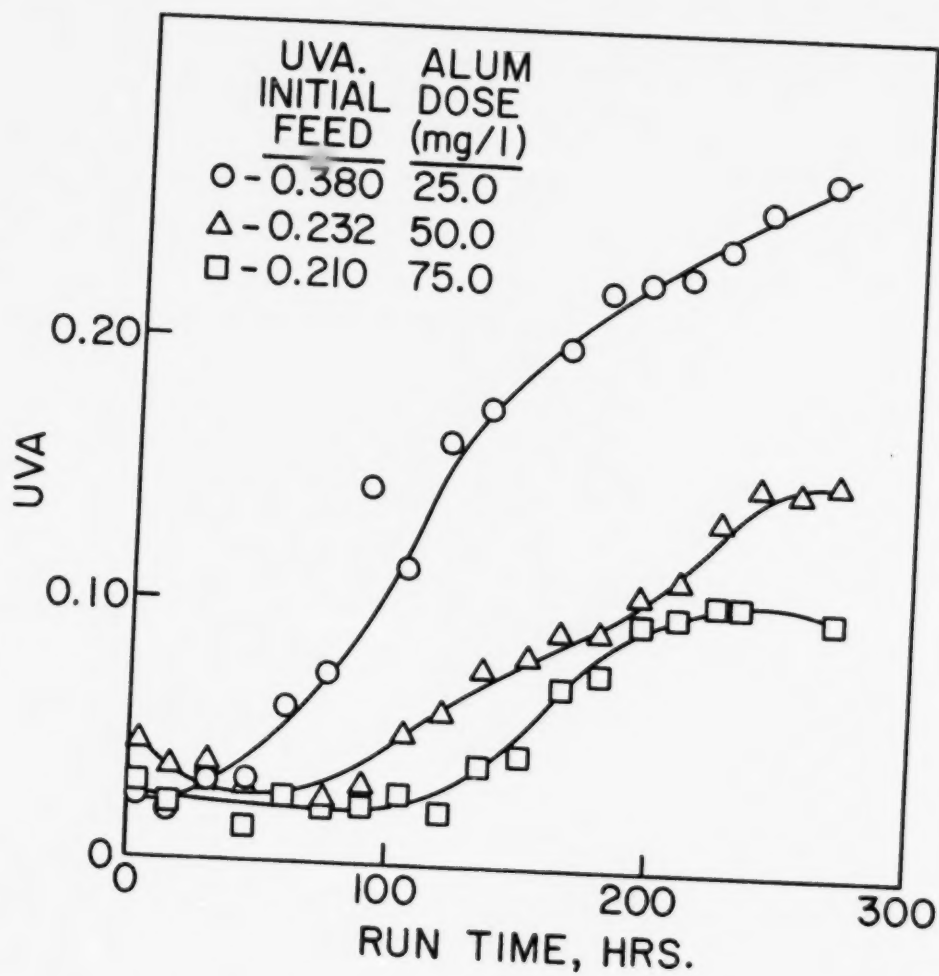


Figure 102. Run C - effect of alum dose on UVA removal by activated carbon at constant adsorption pH = 5.0. Coagulation pH = 5.0; EBCT = 1.15 minutes; flowrate = 3.5 mL/minute.

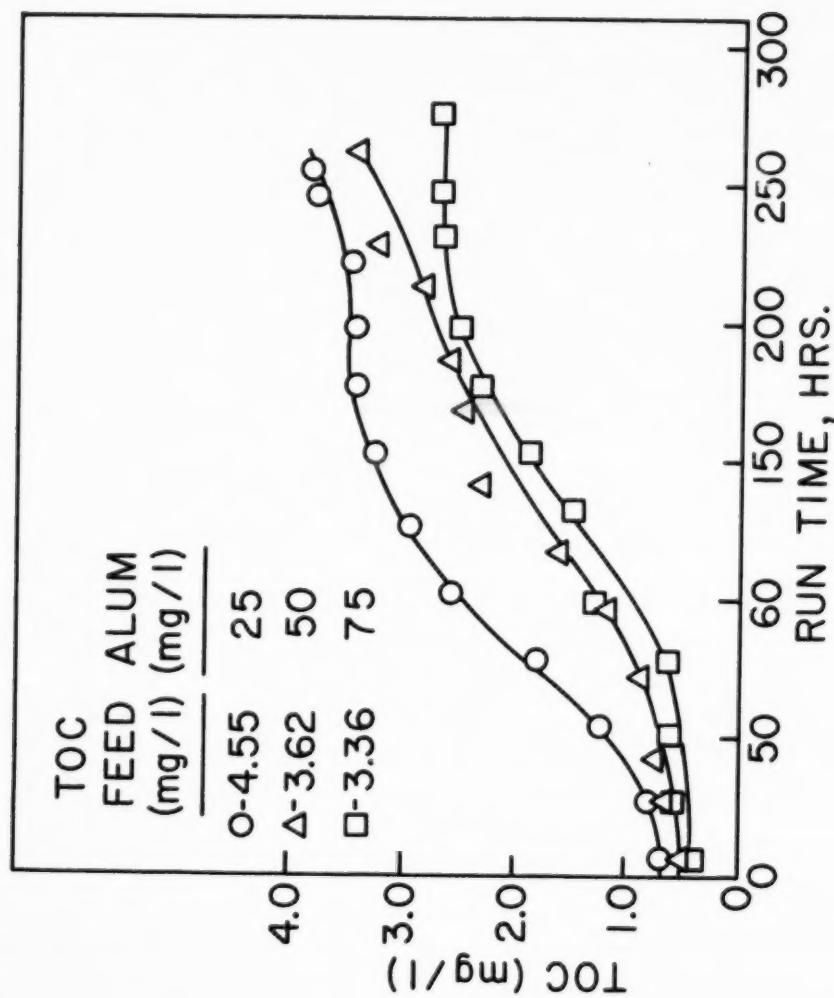


Figure 103. Run C - effect of alum dose on TOC removal by activated carbon at constant adsorption pH = 5.0. Coagulation pH = 5.0; EBCT = 1.15 minutes; flowrate = 3.5 mL/minutes.

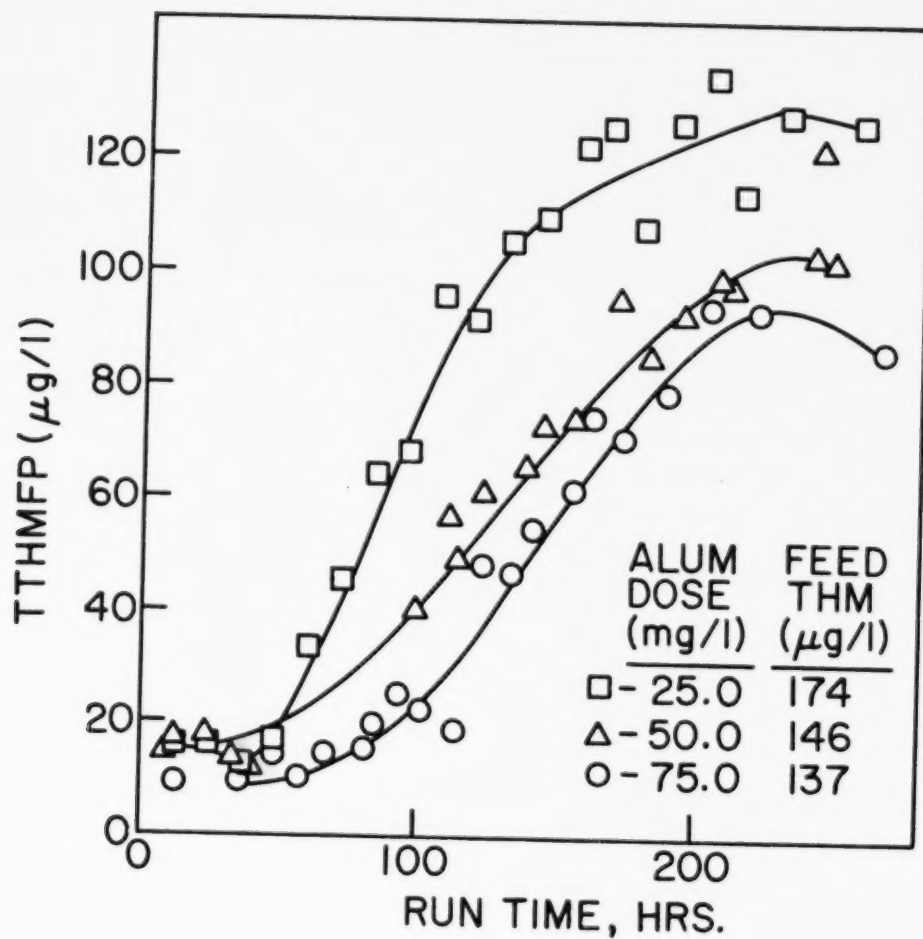


Figure 104. Run C - effect of alum dose on removal of THM precursors by activated carbon at constant adsorption pH = 5.0. Coagulation pH = 5.0; EBCT = 1.15 minutes; flowrate = 3.5 mL/min.

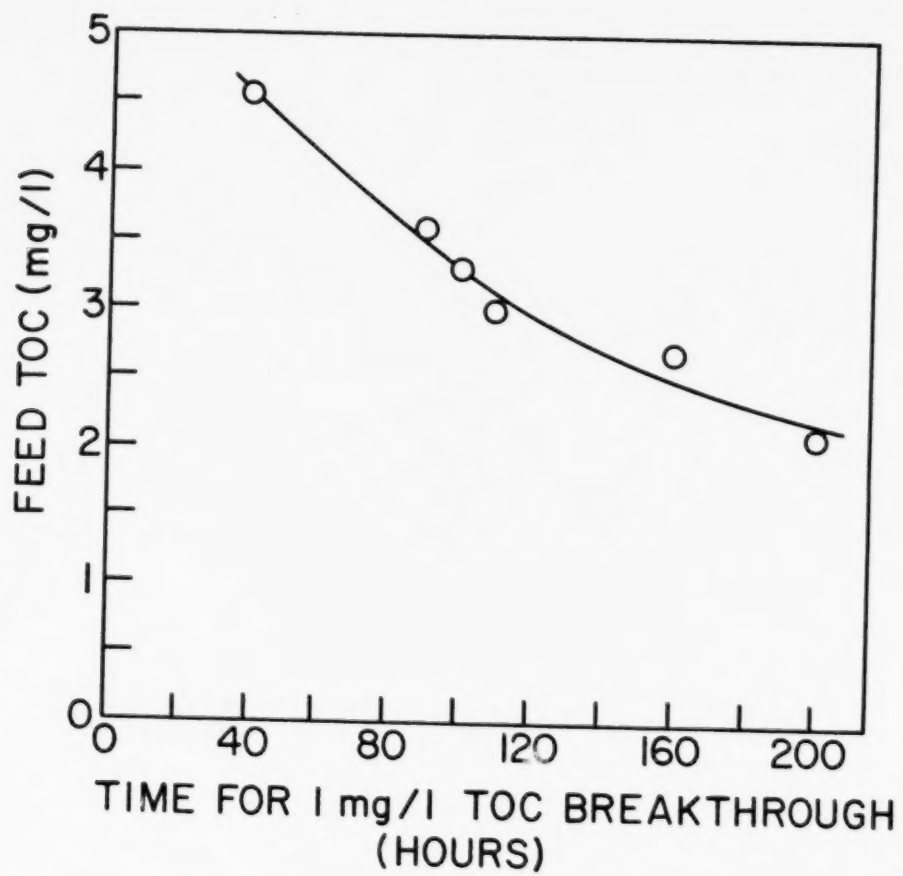


Figure 105. The relationship between influent TOC and carbon service life.

in the neutral range. For example, Getzen and Ward (70) found that the adsorption of several aromatic acids, including phenoxyacetic acid, showed a very strong pH dependence in the pH range from 5 to 9. In this range, the adsorption capacity of phenoxyacetic acid decreased by a factor of 5 as the pH was raised from 5 to 9. However, since the pK_a of the acid is 3.03, the phenoxyacetate ions predominated over this entire pH range. The reduction in adsorption capacity with increasing pH could be explained if weakly acidic functional groups on the carbon surface were dissociating in this pH range, since the increased negative surface charge would reduce adsorption capacity by virtue of increased electrostatic repulsive forces. At the higher pH values, it is possible that OH^- adsorption could also occur, further reducing adsorption capacity. However, Getzen and Ward (70) noted that adsorption capacity for phenoxyacetate was not influenced by pH above 9.0 and it is unlikely, therefore, that significant competitive OH^- adsorption occurred in their study.

Snoeyink *et al.* (72) studied the sorption of p-nitrophenol (PNP) and observed that the capacity of carbon for PNP decreased with increasing pH above that corresponding to the pK_a of 7.15. The decrease in capacity was greater than could be reasonably anticipated from solubility differences and these authors argued that greater electrostatic repulsive forces at higher pH may account for the observed effect. Increased negative surface charge at high pH may have been caused by physical adsorption of OH^- or dissociation of very weakly acidic surface functional groups.

Getzen and Ward (70) also noted that the adsorption of aromatic carboxylic acids was maximized when the solution pH was equal to the pK of the acid. The authors suggested that this may be explained if the presence of undissociated acid enhanced the adsorption of the acid anion. This synergistic effect was discussed in detail in a later paper by the same authors (71).

Other investigators (72,74) have examined the behavior of organic compounds that do not dissociate at low pH. Snoeyink *et al.* (72) observed that phenol adsorption decreased when the pH was decreased from 7.5 to 5.6. The authors argued that since no change in the character of phenol occurred in this pH range, the effect was attributable in part to the competitive effect of the increased quantity of acid sorbed with decreasing pH. They cited evidence that indicated that sorption of phenol on activated carbon surfaces occurs at carbonyl oxygen sites. At low pH, protons may interact competitively with carbonyl oxygen to desorb phenol.

The organic content of the Mississippi River water employed in this study was characterized in some detail by various fractionation procedures detailed in Section 7 of this report. The organics were predominantly lower molecular weight (<10K) compounds having neutral or acidic character. Approximately 60% of the TOC was neutral and 40% was acidic in nature when characterized according to the procedure developed by Leenheer and Huffman (33). The adsorptive behavior of this complex mixture of naturally occurring organics as a function of pH is more difficult to explain than the single solute studies discussed above. However, the single solute studies

provide insights and suggest possible explanations that may help understand the observed behavior.

It is likely that in the range of pH between 5 and 9, both the carbon surface charge and the degree of dissociation of the organic content of water will vary. The carbon surface will become more negative and weakly acidic groups such as phenolic groups on the organics may dissociate, rendering the organics more negative, as pH is increased (76). This will cause an increase in electrostatic repulsive forces which may account for the observed reduction in adsorption capacity.

Black and Christman (77) studied the character of humic substances in colored surface water and found that the humic substance particle size increased and the number concentration of particles decreased as pH decreased. These changes in the character of the naturally occurring organics may be significant. The studies of Ward *et al.* (70,71) and Snoeyink *et al.* (72) both suggest that in this pH range it is likely that the change in the character of the carbon may be more significant than any change in the character of the organics.

The influence of pH on TOC removal from river water may vary for different carbons and even for the same carbon following regeneration. Coughlin *et al.* (73) showed that the carbon surface functional groups may have a significant impact upon adsorptive capacity. For example, carboxylic functional groups tended to reduce the adsorption capacity of carbon for phenol. Different carbons, as well as the same carbons, exposed to different solution conditions, may have different surface concentrations of functional groups. For example, exposure of a carbon to either OCl^- or permanganate, both of which may be used in a water treatment plant, may increase the concentration of surface carboxyl groups. These changes in the surface chemistry of carbon may be expected to cause different responses to changing pH conditions for a given water.

The cation composition of the pretreated waters was not significantly influenced by the pH adjustments in the range considered. Although divalent metal ions such as Ca^{++} and Mg^{++} may influence the extent of organics adsorbed, these ions were always present in concentrations greater than 10^{-3}M (even following softening pretreatment) and Randtke *et al.* (75) found that these ions only had a significant impact on organics adsorption when their concentration fell below 10^{-3}M . It is unlikely, therefore, that any change in the Ca^{++} or Mg^{++} composition could have significantly influenced adsorption behavior in the pretreatment studies.

Optimum pH

The influence of pH adjustment upon carbon column performance is sufficiently great that it may be beneficial for a water treatment facility to consider pH reduction prior to GAC. To avoid corrosion problems in the distribution system, the GAC treated water would need to be stabilized by

alkalinity addition. The cost of pH control is, therefore, the combined cost of acid addition to reduce pH and alkalinity addition for the restoration of a stable pH following GAC treatment. The cost of GAC treatment decreases as the bed life of the carbon is extended for a given treatment objective and it will, therefore, decrease as pH is decreased. It is likely, however, that an optimum pH exists to minimize the overall cost of water treatment. Below this pH value, the cost of additional acid and base addition will exceed the benefit to be gained from extended carbon life.

Consider a simple example calculation for the optimum operating pH for the minicolumns based upon the performance curves depicted in Figure 93. Assume: 1) The capital costs of the carbon columns and pretreatment operations are independent of operating pH; 2) only chemical costs are considered in this analysis; 3) treatment objective is < 1 mg/L TOC in the GAC column effluent; 4) the system is closed (no CO_2 escapes when acid is added to water); 5) all the alkalinity is present as bicarbonate.

Let H = cost of H_2SO_4 (\$/lb.)

N = cost of NaOH (\$/lb.)

$[A]$ = alkalinity (eq/L)

$[H^+]_0$ = initial hydrogen ion concentration (moles/L)

$[H^+]_F$ = final hydrogen ion concentration (moles/L)

$[L]$ = acid added eq/L

The cost of pH control, $C_{\text{pH}} = C_{\text{acid}} + C_{\text{base}}$

where

C_{acid} = cost of acid required to drop pH to desired level/
unit time

C_{base} = cost of base required to raise pH to level for distribu-
tion/unit time

$$C_{\text{pH}} = \frac{Q \cdot L \cdot M_A}{454} + \frac{Q \cdot L \cdot M_B \cdot N}{454} \quad (9)$$

where M_A and M_B are the equivalent weights of acid and base, respectively, and where the base addition is that required to neutralize the added acid. Q is the flowrate of water treated. The added acid will reduce the pH and improve GAC service life. The improvement will lead to a lower carbon cost which may be computed. Assume $[L] < [A]$ and the pH level to which a water will drop may be calculated from a consideration of the carbonate equilibria, viz:

$$[H^+]_F = \frac{L \cdot 10^{-6.3}}{[A \cdot L]} + \frac{[H^+]_0 A}{[A - L]} \quad (10)$$

From Figure 93 a relationship may be derived to relate service time, T (hours), to the operating pH for a specific treatment objective. Assume, for example, that the treatment objective is < 1 mg/L TOC in the effluent at all times, then the data in Figure 93 fit the equation:

$$T = 47(10.05 - \text{pH}_F) \quad (11)$$

for the pH range 5.0 - 8.7. Substituting for pH_F in equation 11 yields the following expression in which T is a function of the amount of acid added to the water:

$$T = 47(10.05 + \log(\frac{[L]10^{-6.3}}{[A-L]} + \frac{[H_O^+][A]}{[A-L]})) \quad (12)$$

The cost of the activated carbon per unit time, C_c , may be estimated by dividing the cost of the carbon used in a column by its service life, T (hours). The cost of the carbon is equal to $V\rho M$ where V is the carbon bed volume (ft^3), ρ is the packed bed density of the carbon (lbs/ft^3) and M is the carbon cost ($\$/\text{lb.}$)

$$\therefore C_c = \frac{V\rho M}{T} \quad (13)$$

By combining the costs of acid and base addition with the cost of carbon treatment the overall cost may be developed. Combining equations 10, 12 and 13 the overall cost function, C_T , may be written:

$$C_T = \frac{Q \cdot [L] \cdot M_A \cdot H}{454} + \frac{Q \cdot [L] \cdot M_B \cdot N}{454} + \frac{V\rho M}{47(10.05 + \log(\frac{[L]10^{-6.3}}{[A-L]} + \frac{[H_O^+][A]}{[A-L]}))} \quad (14)$$

In this expression, it should be recognized that Q and V are not variables. This is because the relationship for T (equation 11) is specific for the flowrate and column size studied. If more data were available interrelating the empty bed contact time, pH and service life for the GAC columns, then T could be expressed as a function of the variables, V, Q and pH for a given treatment objective. Additional studies are needed in this area.

TABLE 16. DATA EMPLOYED FOR OPTIMUM pH CALCULATION

$[A] = 2 \times 10^{-3} M$	$M_B = 40$
$N = \$0.10/\text{lb.}$	$V = 2.07 \times 10^{-4} \text{ ft}^3$
$H = \$0.10/\text{lb.}$	$\rho = 30 \text{ lbs}/\text{ft}^3$
$M = \$0.85/\text{lb.}$	$[H_O^+] = 10^{-8.3}$
$M_A = 98$	$Q = 0.210 \text{ liters}/\text{hr}$

By substituting the data in Table 16 into the cost function, the overall cost of treatment could be calculated as a function of the amount of acid

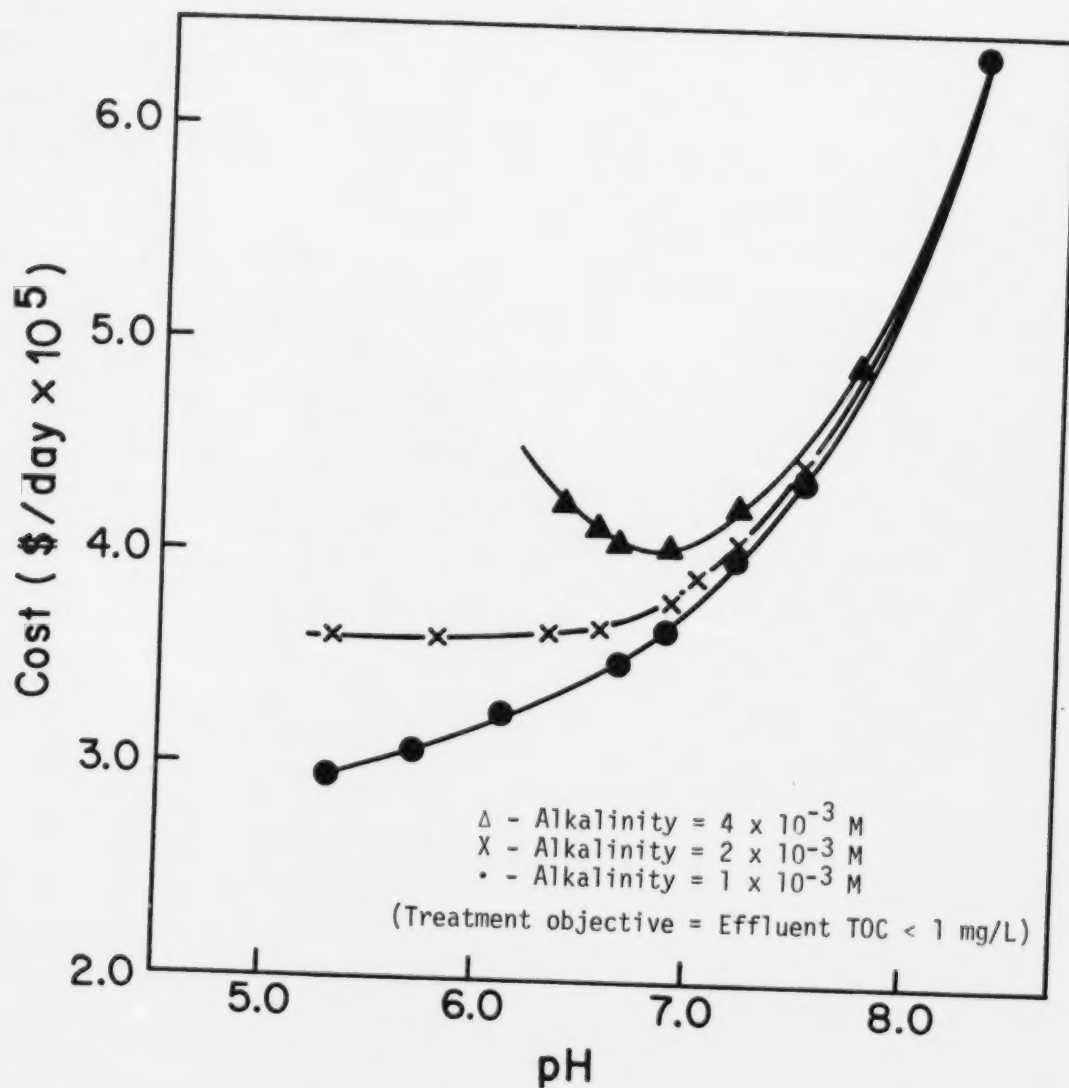


Figure 106. Calculated cost per day of operating the minicolumn as a function of operating pH.

added (L) or the operating pH (pH_p). The optimum pH is dependent upon the relative costs of acid, base and carbon and also upon the alkalinity of the water being treated. As the alkalinity is increased, the optimum pH will increase also since the cost of reducing the pH increases. In addition, however, the shape of the cost-function is altered as shown in Figure 106. When the alkalinity is low ($10^{-3}M$) an optimum pH was not identified but rather the cost of treatment continued to decrease as the pH decreased. In such cases the operating pH should be as low as possible within the constraints imposed by materials of construction. When the alkalinity is somewhat higher ($2 \times 10^{-3}M$), the cost function indicated that a significant benefit was to be gained by reducing the pH from 8.3 to 7.0 but no significant cost reduction was gained by operating at lower pH values. In the last case considered, an alkalinity of $4 \times 10^{-3}M$ (200 mg/L as $CaCO_3$) caused the cost function to exhibit a well-defined optimum pH at about pH 6.8.

This type of analysis is valuable for identifying the importance of pH as an operating parameter in water treatment plants where carbon adsorption is to be implemented. While the results of this analysis cannot be extended to the treatment of other waters, the same approach may be applied to identify the best operating conditions.

The assumption of a closed system is probably fair since the conditions in a flocculation tank are not conducive to the loss of CO_2 . The small air/water interface and the gentle mixing conditions prevent a major loss of CO_2 from the water. However, it should be noted that the pH of the water may be raised following carbon adsorption by stripping the CO_2 from solution. This process would serve to reduce the base requirement for pH stabilization and it may also serve to reduce the concentration of low molecular weight volatile organics in the product water.

Influence of Coagulation

As noted above, the impact of operating pH upon carbon service life is dramatic and improved performance and lower cost treatment may be achieved at lower pH values. The tests on the impact of coagulation in this study were purposefully conducted at a fixed pH to eliminate the pH effect from studies on the impact of coagulant dose. In practice, however, the added coagulant would reduce solution pH. Alum and ferric sulphate contribute 6 equivalents of hydrogen ion to solution for each mole added. In the case of alum, for example, this means that approximately 1 equivalent/L of hydrogen ion was added for each 100 mg/L dose. The amount of hydrogen added is, therefore, not insignificant to the analysis of the pH effect for Mississippi River water samples tested in this study, and it would tend to reduce the cost of acid addition and lower the optimum pH during pretreatment.

Previous investigators have identified the benefits to be derived from coagulation as a pretreatment for activated carbon adsorption (75,78,79). Randtke et al. (75) observed that coagulation significantly increased the adsorptive capacity of activated carbon for the remaining TOC, except when little or no TOC removal occurred during the coagulation process. This improvement was attributed to an interaction between the aluminum species

and the remaining organic molecules. Randtke discussed other effects that may account for the observed behavior, such as lower initial TOC concentrations for the adsorption studies on coagulated water; preferential removal of weakly adsorbing organics during the coagulation process, and changes in the ionic strength or composition of the water. However, using experimental evidence cited in their article, they contended that these explanations could not account for the observed behavior and therefore concluded that the formation of aluminum-organic complexes was the major contributing factor to improved organics adsorption.

The exact mechanism by which alum improved the adsorption capacity of carbon was not clear, however, and the authors acknowledged the need for additional studies in this area. Part of the difficulty in explaining the observed behavior was the fact that aluminum did not improve carbon adsorption capacity until a certain alum dose had been applied. The effective dose was somewhat less than the stoichiometric requirement for systems showing type I behavior or sufficient to cause a significant amount of TOC reduction ($\sim 30\%$) in systems exhibiting Type 2 behavior. If aluminum associates with the organic content of the water to improve its adsorbability, it is not clear why lower aluminum doses are ineffective in improving adsorption.

Lee et al. (78) also tested the influence of alum pretreatment on the adsorption behavior of peat fulvic acid. They concluded that alum coagulation enhanced both carbon adsorption capacity and the rate of uptake. However, the increased capacity was thought to be the major effect contributing to longer carbon column service life.

An earlier study by Sontheimer and Maier (79) also indicated that coagulation of Rhine River water (following bank filtration and ozonation) improved the adsorption behavior of the water. The residual organic content was better adsorbed than the original organic content of the water. In addition, these authors observed that the adsorbability of the residual organics was better following aluminum sulphate coagulation than ferric chloride pretreatment.

The characterization studies presented in Section 6 of this report provide a useful basis for examining the effectiveness of different pretreatments on residual organic matter. The results indicated that higher molecular weight organic compounds were preferentially removed during coagulation and that lower molecular weight compounds were largely unaffected. The residual organic compounds were classified as predominantly hydrophilic acidic and neutral in character using the Leenheer-Huffman fractionation procedure (33). The detailed results are presented in the discussion section at the end of Section 6. These results strongly suggest that it is the ability of coagulation pretreatment to remove the higher molecular weight compounds that contributes to improved carbon adsorption of the residual organics. Many investigators have observed that higher molecular weight compounds are not as well removed by activated carbon (78,80). Lee et al. also observed that the higher molecular weight fraction of a peat fulvic acid exhibited the same adsorption capacity as the unfractionated material. This

suggested that the higher molecular weight fraction controlled the observed adsorption capacity in the unfractionated fulvic acid and the authors invoked an association between the lower and higher molecular weight fractions in the unfractionated mixture to explain this behavior. Thus, coagulation removes the weakly adsorbing high molecular weight fraction of the organic content and leaves the strongly adsorbing low molecular weight fraction in solution. The lower average molecular weight of the organics in solution following coagulation will also contribute to improved adsorption kinetics as observed by Lee et al. (78).

In this study it was felt that the major improvement in adsorption capacity following coagulation was caused by the removal of weakly adsorbing organics and not by an association of the coagulant with the organics. Earlier studies by Semmens and Field indicated that the residual aluminum concentration in the coagulated waters was a function of pH and independent of coagulant dose in the dosage range of practical application suggesting that association between aluminum and the residual organics in solution was not dependent upon coagulant doses. In this regard, the authors conclusions differ from the conclusions drawn by Randtke et al. (75). However, Randtke did not demonstrate that aluminum-organic association occurred in his study, but rather he invoked this association to explain the results after disproving alternative explanations.

However, regardless of the exact mechanism involved, coagulation pretreatment has a major role to play in the optimization of organics removal in facilities employing or intending to employ activated carbon. The effective reduction of humic substances in a carbon column influent is likely to increase the carbons effective capacity for specific organic contaminants because of the reduced competition. However, this requires verification in future research studies.

Optimum Coagulant Dose

The impact of coagulation pretreatment was evaluated over a one-year period with three different river water samples. In each case the dose response of the water for organics removal by coagulation was different. In one sample removals increased up to an alum dose of > 200 mg/L, another sample showed a plateau in organics removal at about 90 mg/L and the third sample exhibited intermediate behavior. Nevertheless, the adsorption behavior of the organic content of each water sample was improved by coagulation pretreatment to a similar extent, and the service time to 1 mg/L TOC breakthrough could be correlated with the TOC in the carbon column feed. The useful life of a carbon column may, therefore, be correlated indirectly with the coagulant dose employed during pretreatment for a specific water sample. For example, for the water sample tested in Run C it is possible to develop the correlation between service time and coagulant dose by using the jar test data in Figure 101 and the correlation in Figure 105. The data presented below in Table 17 was extracted in this way. This data was modeled with an equation of the form $\ln(D/D_0) = kT$ where k and D_0 are constants with values equal to 0.0193 and 11.5, respectively, D is the coagulant dose (mg/L) and T is the breakthrough time (hours).

TABLE 17. RELATIONSHIP BETWEEN COAGULANT DOSE AND SERVICE TIME FOR 1 mg/L TOC BREAKTHROUGH

Coagulant Dose mg/L	Breakthrough Time (Hours)
25	40
50	86
75	100
100	112

This type of correlation may be usefully employed to identify the optimum degree of pretreatment that will yield the desired water quality at a minimum cost. The optimum coagulant dose may be calculated in the following fashion: the total operating cost of water treatment is assumed to be equal to the chemical costs for coagulation plus the cost of carbon replacement in this analysis. It is assumed that the power costs and capital recovery costs are independent of the coagulant dosage in the range of dosages considered.

The coagulation cost (\$/time) may thus be represented by an expression of the type

$$C_{\text{COAG}} = \frac{DQB}{4.54 \times 10^5} \quad (15)$$

where

D = coagulant dose (mg/L)
Q = flowrate (liters/hr)
B = cost of coagulant (\$/lb)

The carbon cost may be similarly estimated:

$$C_{\text{GAC}} = \frac{V\rho M}{T} \quad (16)$$

where

V = volume of carbon bed (ft³)
ρ = packed bed density of carbon (lbs/ft³)
M = carbon cost (\$/lb)
T = service time to 1 mg/L breakthrough (hrs)

$$\text{Total cost} = C_{\text{COAG}} + C_{\text{GAC}} = C_T$$

$$C_T = \frac{DQB}{4.54 \times 10^5} + \frac{V\rho M}{T} \quad (17)$$

substituting for T

$$C_T = \frac{DQB}{4.54 \times 10^5} + \frac{V_p M (0.0193)}{\ln(D/D_o)} \quad (18)$$

For minimum total cost $dC_T/dD = 0$

Differentiating equation 18 and simplifying, the resulting expression is obtained:

$$\frac{dC_T}{dD} = \frac{QB}{4.54 \times 10^5} - \frac{0.0193 V_p M}{D (\ln(D/D_o))^2} \quad (19)$$

The coagulant dose required to minimize treatment costs is, therefore, given by setting equation 19 to zero and rearranging:

$$D (\ln(D/D_o))^2 = \frac{8.76 \times 10^3 V_p M}{QB} \quad (20)$$

The optimum coagulant dose may be estimated using equation 20. It is noteworthy that the coagulant dose is dependent on the relative costs of carbon and the coagulant. As the ratio of carbon cost to coagulant cost increases, the optimum coagulant dose will also increase. The optimum dose is also apparently related to V/Q , or the empty bed contact time (EBCT). However, because of the way in which the relationship between service life and coagulant dose was developed from operational data, the EBCT is not a variable. For different EBCT's the dose-service time relationship would vary.

Substituting actual operating data from the minicolumn study and current cost data (November 1981) as listed in Table 18, the optimum coagulant dose was calculated to be 46 mg/L alum.

TABLE 18. DATA EMPLOYED IN THE CALCULATION OF OPTIMUM COAGULANT DOSE

$C = \$0.10 \text{ lb. (1)}$	
$Q = 0.210 \text{ liters/hr.}$	
$V = 2.07 \times 10^{-4} \text{ ft}^3$	
$\rho = 30 \text{ lbs/ft}^3$	
$M = \$0.85/\text{lb. (2)}$	
(Westvaco WV-G)	
(1) Bulk shipment cost to Minneapolis - Figures from Municipal Water Treatment Plant Nov. 1981	
(2) Bulk shipment (>32000 lbs) Cost to Minneapolis, Courtesy Westvaco, Covington, VA, Nov. 1981	

If the treatment objective was not $< 1 \text{ mg/L}$ effluent TOC, then the above optimization would be invalid. For different treatment objectives, the correlation between coagulant dose and service time must be redetermined and the

resulting cost function must be minimized. One would anticipate that the optimum coagulant dose would be reduced as the allowable carbon column effluent TOC is increased since the rate of carbon consumption decreased for a given coagulant dose. However, the observed tendency of the pretreated waters to plateau at lower effluent TOC values as coagulant dose increased may influence this analysis. For example, if a treatment objective of 3 mg/L is selected for the effluent TOC, then Figure 103 suggests this could be achieved with 75 mg/L alum pretreatment, and the carbon might never need replacement. Naturally, much longer run times would be needed to more precisely evaluate such a possibility.

In addition, the above analysis was presented for a constant pH condition and in actual practice the solution pH is influenced by the coagulant dose.

SYNTHETIC RESIN PERFORMANCE COMPARED TO CARBON

Literature Review

Ion exchange resins have been evaluated for their ability to remove organics from water by many investigators. The effectiveness of a resin is influenced by many factors including the nature and source of the organic compounds in the water (82), the degree of pretreatment (84), the solution composition and pH (82), and, finally, the properties of the resins themselves (83,85).

The removal mechanism is primarily ion exchange, although, under certain conditions, hydrogen bonding has been invoked to explain organic removal behavior. In the removal of organics by ion exchange resins, many factors may be influential in determining the extent of removal. With the exchange of inorganic anions, the removal effectiveness is controlled by three primary factors: 1) ionic charge, 2) ion size and 3) ionic hydration energy (86). In the case of organic ion exchange, additional important factors contributing to removal include: 4) interaction between the organics and the polymer matrix of the exchange resin and 5) organic-organic interactions within the resin phase. For example, the removal of aliphatic acid ions from solution at neutral pH by a strongly basic anion exchanger will be best for the acid anion having the highest molecular weight (87). This is because all the ions have the same degree of electrostatic interactions but as the hydrocarbon chain of the ion increases, with a corresponding increase in molecular weight, the opportunity for favorable interaction with the polymeric matrix is increased and hydrophobic bonding may occur (85,87). In an acrylic strong base resin fatty acid anions were observed to interact with each other when the internal concentrations of the acids exceeded (87) their critical micelle concentrations.

In natural waters, the large polyanionic humic and fulvic acids may thus be removed very effectively via exchange and adsorptive forces. There is a desirable balance, however, between removal effectiveness and regeneration efficiency in ion exchange resin selection because resins that are highly effective in removing organics are of little value if they cannot be regenerated efficiently. Regeneration of ion exchange resins may also be hampered

by the physical contraction of the resins in concentrated regenerant solutions. The exchange process is diffusion controlled, and if the resin shrinks significantly during the course of regeneration, the ability of fulvic and humic acids to exit the resin structure may be impaired. Early studies on the use of gel-type resins in water treatment showed that these resins could not be effectively regenerated and became fouled with organic materials (81). This led to the development of Macroporous resins that were designed to have pores large enough to easily accommodate humic and fulvic acids with a more rigid structure that contracted less during regeneration. These resins are, therefore, less susceptible to organic fouling and are preferred in water treatment applications.

The functional groups of the resins are influential in determining both organic removal behavior and regeneration efficiency. Because the organics in water are typically anionic or neutral in character, most investigators have selected either anionic or non-ionic resins for comparison with activated carbon. Non-ionic resins have no substituted functional groups on the polymer matrix and organics are removed by adsorption to the matrix structure.

Previous studies on the relative performance of non-ionic resins such as XAD 2 and XAD 8 (Rohm and Haas) versus activated carbon indicate that these resins do not have as large a capacity for organics removal as activated carbon. The non-ionic resins can be regenerated efficiently with organic solvents. Although they have great value in research for isolating organics (88) from water, these resins are unlikely to find application in water treatment practice. More recently, Rohm and Haas introduced an experimental non-ionic resin, Amborsorb XE 340, which is selective for low molecular weight chlorinated organics. This resin is still being tested but recent publications suggest that this resin is effective for removal of compounds such as trichloroethylene (TCE) and that it is effectively regenerated by steam stripping (89) but the presence of TOC in the column influent reduced the effectiveness of TCE removal.

Weakly basic resins have been studied for organics removal in water treatment by several investigators (82,91,92). The removal behavior of these resins is strongly pH dependent (85,93). At low pH values the amine functional groups are protonated and the resin functions as an anion exchanger, but at pH values exceeding the pK of the functional groups (approximately 6), the functional groups revert to the free base form and the resin becomes non-ionic. It is this feature of weakly functional resins that enables them to be regenerated almost stoichiometrically. These resins may remain effective for removing organic anions in the neutral pH range by mechanisms such as hydrogen bonding to the amine groups or by adsorption to the resin matrix; however, the resins' capacity for organics removal is considerably less when it is in the free base form (93,94). In the acid form, the capacity of a phenol formaldehyde resin has been shown by Hinrichs *et al.* (93) to be better than, or comparable to, that of activated carbon for several organics solutes. However, even in the free base form high capacity weakly basic phenol formaldehyde resins such as Duolite A7 (Diamond Shamrock) have been shown to be as effective for removing commercial humic acids as is activated carbon (82), and they were also shown to be effective for removing humic

acids from Rhine River water (92).

Strongly basic anion exchangers are not influenced by pH in the practical range of interest, and these resins have been shown to be very effective for removing organics from natural waters. Macko tested a selection of macroporous resins and found the strongly basic resins were most effective for removing organics from Mississippi River water and removed over 90% of the river water TOC (69). Amberlite 904 was found to be the most effective of the resins tested, and it was regenerated effectively with a 1 normal (1N) sodium chloride brine. Kolle also found a strongly basic resin was effective for removing about 50% of the TOC from colored groundwater for up to 5000 bed volumes of throughput (95). In addition, the resin could be regenerated effectively with 2 bed volumes of a mixed 4.5N brine containing NaOH and NaCl. Neither of these studies conducted long-term repetitive tests to identify problems related to fouling and incomplete regeneration and further work is needed in this area. Gauntlett (83) found evidence that specific organic compounds were not completely removed from a strong base resin during regeneration but the results were inconclusive.

Experimental

A column study was conducted to compare the performance of synthetic resins with activated carbon for removing organics from pre-treated river water. A sixty gallon river water sample was collected and coagulated at approximately pH 7.0 with 50 mg/L of alum. The same filtered pre-treated water was then fed to each of four minicolumns. The exact column procedure was as described above in the section on experimental methods. The resins were sieved to the same mesh (50x80) as the carbon and the bed volumes of the four columns were identical (6.4 cm³). The resins were washed initially with warm distilled water then with approximately 40 mL of methanol and finally followed by an additional distilled water rinse for 15 minutes. Both weakly basic resins were in the free base form at the start of the column study.

The feed solution was adjusted to pH 7 and pumped at a rate of 3.5 mL/minute to each column to provide an EBCT - 1.84 minutes and effluent samples were collected manually twice a day. The effluent samples were acidified to pH 4 with H₂SO₄ and tested for UVA, TOC and THM precursor concentrations.

The resins selected were those resins which were found to be promising by previous investigators. Boening and Snoeyink (82) and Macko (69) found IRA 904 (Rohm and Haas) very effective in organics removal from water. The former authors also found that among the weak base resins, Duolite A7 (Diamond Shamrock) gave quite good performance in the neutral pH range. The third resin, another weak base resin, Duolite S37 (Diamond Shamrock), was run for comparison with the A7 resin. The results are shown in Figure 107, 108 and 109. It was apparent that the weak base resins Duolite A7 and S37 were not as effective as IRA 904 and carbon. The latter columns compared very favorably and IRA 904 was essentially just as effective as the carbon tested (Westvaco WV-G). The results indicate that IRA 904 may be competitive with activated carbon as an adsorbent. The tests were run for up to 800 hrs.

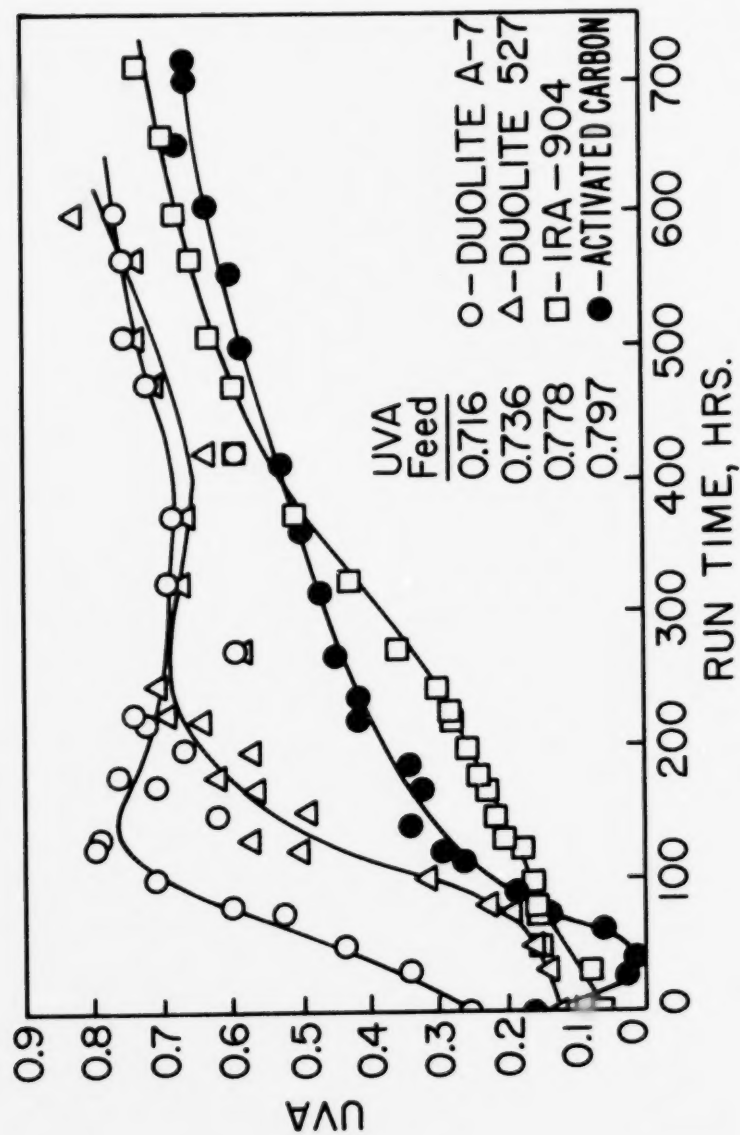


Figure 107. UVA removal by carbon and synthetic resins - Run 1.
 Feed = river water coagulated with 50 mg/L alum at pH 7.0.
 Adsorption pH = 7.0, EBCI = 1.84 minutes, flowrate = 3.5 mL/min.
 Influent UVA = 0.716-0.797.

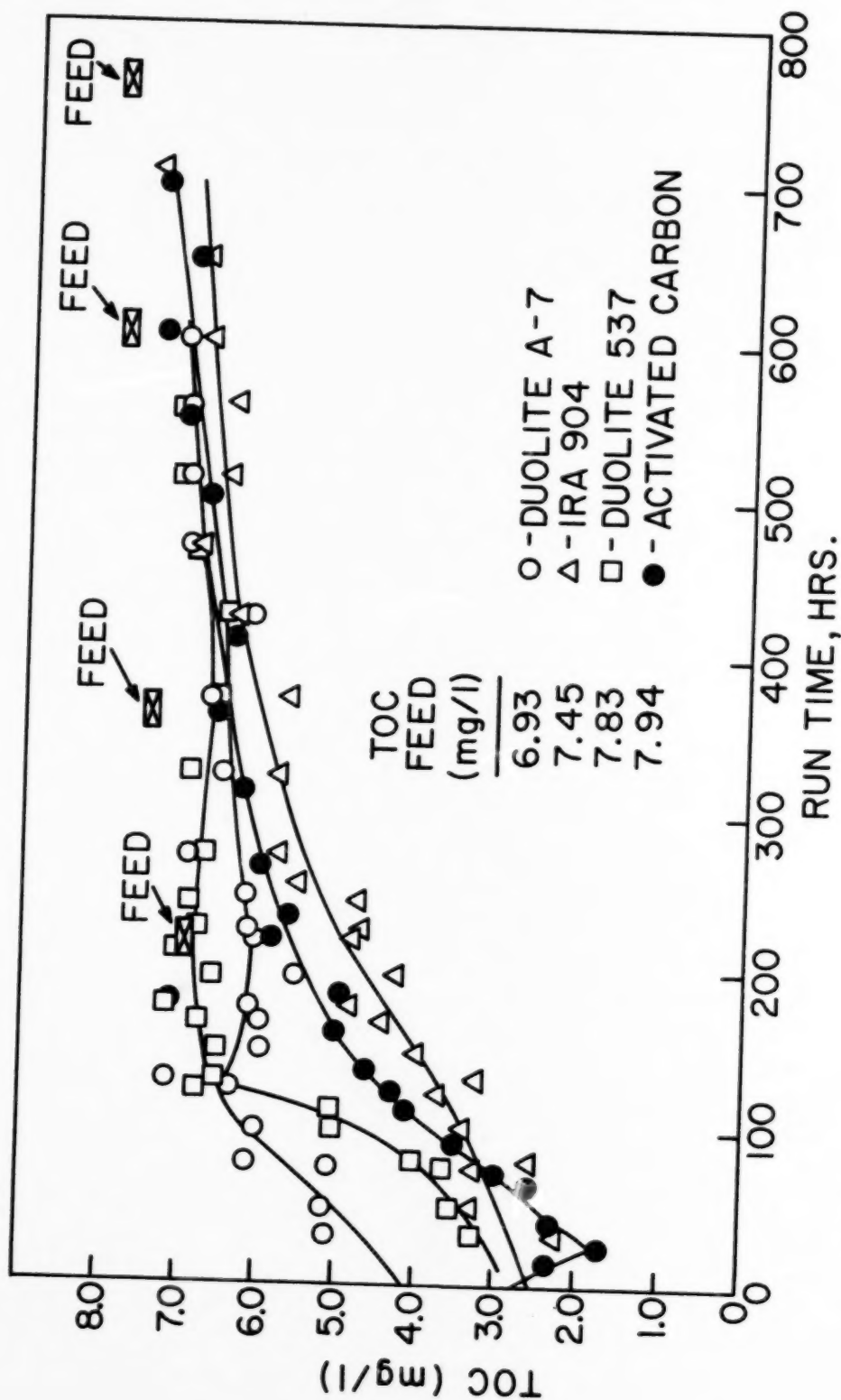


Figure 108. TOC removal by carbon and synthetic resins - Run T.
 Feed = river water coagulated with 50 mg/L alum at pH 7.0.
 Adsorption pH = 7.0, EBC = 1.84 minutes, flowrate = 3.5 mL/min.
 Influent UVA = 0.716-0.797 Feed TOC = 6.9-7.9 mg/L.

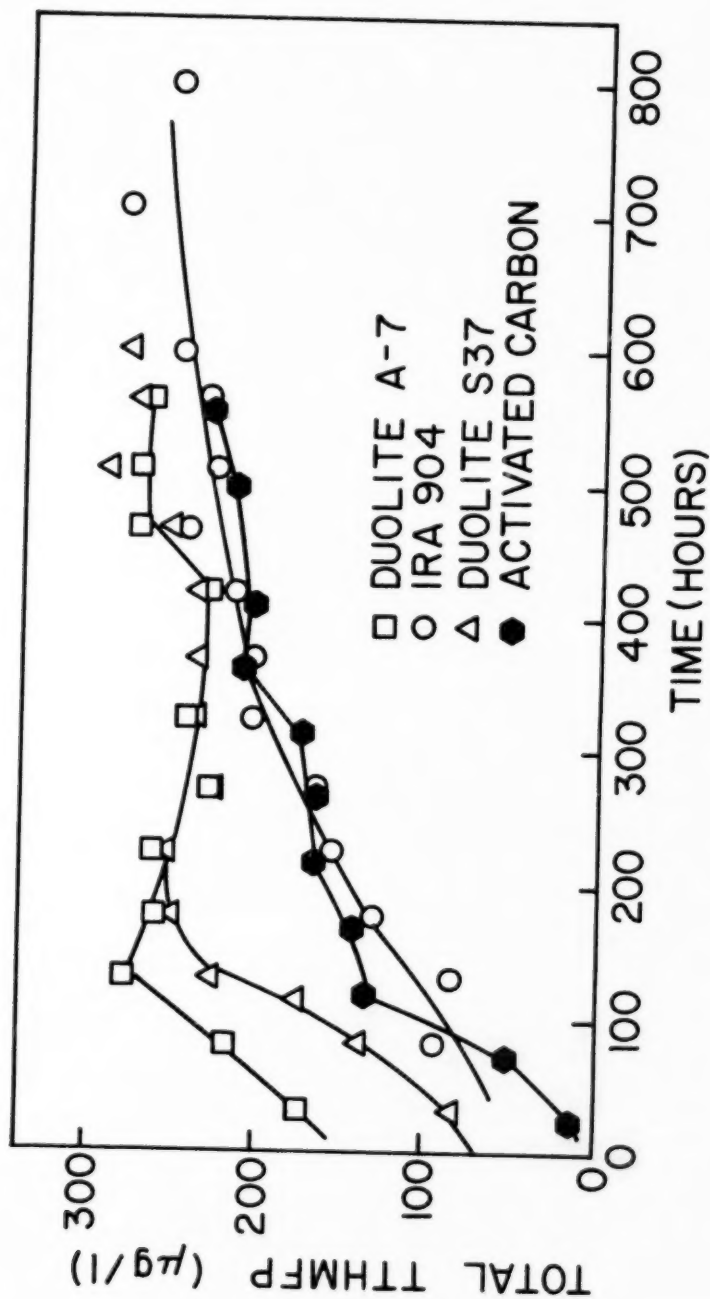


Figure 109.

TTHMFP removal by carbon and synthetic resins - Run T.
 Feed = river water coagulated with 50 mg/L alum at pH 7.0.
 Adsorption pH = 7.0, EBCT = 1.84 minutes, flowrate = 3.5 mL/min.
 Influent UVA = 0.716-0.797. Feed TTHMFP =

and, interestingly, the final effluent quality was similar for both the carbon and IRA 904.

Following the column breakthrough study, the IRA 904 resin was flushed with 1N NaCl downflow at 3.5 mL/min (EBCT - 1.85 mins). The sodium chloride regenerant was effective in stripping organics from the exchange resin and the spent regenerant was highly colored. The effluent TOC during regeneration is plotted in Figure 110 and shows a typical elution profile with very large concentrations of TOC released initially and a slower release as regeneration progressed. A mass balance on TOC was not conducted in this study. Some fouling and loss of capacity may occur when anion exchangers are employed to treat natural waters and complete regeneration may not be obtained (81). Macko (69) studied the use of IRA 904 for organic removal from river water and found that the extent of organics displacement was close to 100%. Repetitive cycling studies with practical regeneration conditions were not run, however, and under such conditions of use, the resin performance may deteriorate with time.

These results for the use of resins are encouraging. It was apparent that even though the river water had received coagulation pretreatment, the resins were able to remove additional TOC and THM precursors. The weakly basic resins Duolite S37 and A7 did not perform as well as the strongly basic resin tested, but these studies were conducted at pH 7, and perhaps these resins may be more effective when tested at different pH values. Boening (82) studied the influence of pH on the sorption of commercial humic acid by Duolite S37 and found that sorption was best at pH 8.3 and diminished at higher and lower pH values. Although the pH dependence of sorption is dependent upon the character of the organics being removed, it is reasonable to assume that the commercial humic acids tested by Boening (82) may reflect behavior of organics in a colored surface water like the organics tested in this study. Interestingly, however, Boening found A7 to be superior to S37 and comparable to activated carbon for removing commercial humic acids, and yet in the application of these resins to pretreated Mississippi River water, the A7 exhibited poorer removal performance than S37. Both resins were inferior to activated carbon.

The performance of IRA 904 was impressive and verifies the results of Macko (69). Although Macko did not pretreat the river water, the IRA 904 was able to remove almost all the TOC from raw river water at the beginning of a column run. Pretreatment was, therefore, instrumental in decreasing the organic load to the ion exchanger and increasing the effective service life of the column. This result contrasts with the observations of Symons et al. (89) who found that IRA 904 removed 30% of the TOC and about 50% of the THM precursors from a groundwater, but after lime softening pretreatment of the water, the resin was unable to reduce the THM precursor concentration. At the present time, there is very little published data on the influence of pretreatment upon resin adsorption behavior and more studies are needed in this area.

The IRA 904 resin was as effective as activated carbon for removing organics in this study, and since it may be regenerated effectively with

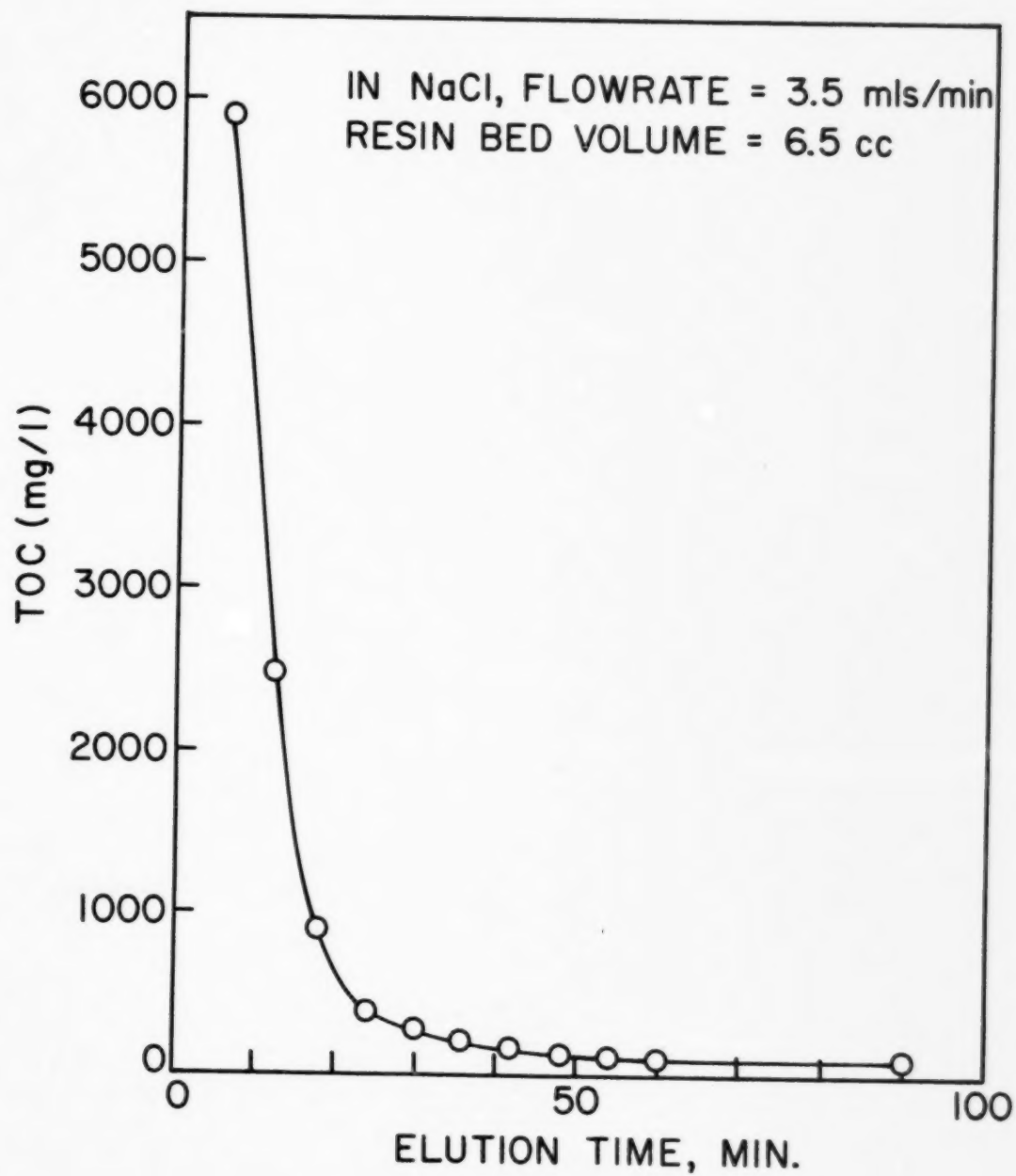


Figure 110. Total organic carbon vs elution time for Duolite 904 resin during regeneration with 1N NaCl.

sodium chloride brine, it warrants further consideration. The choice of regeneration conditions was arbitrary and it is likely that with higher regenerant brine concentrations, the resin may be regenerated more efficiently. For example, Kolle used a regenerant containing 100 grams/liter of NaCl and 20 g/L of NaOH and found that, with careful reuse, a very small volume of highly concentrated spent regenerant was generated. Further studies are obviously needed on this subject.

Lime Softening

In an initial evaluation on lime softening as a pretreatment process a comparative study was conducted to compare different softening approaches to coagulation with alum. In this study a water sample was collected from the Mississippi River. On the same day and at approximately the same time the river water was sampled at the point of extraction. Three samples of pretreated water were prepared and compared to the pretreatment given by the Minneapolis water treatment plant.

The water sample taken within the plant had been softened by addition of 130 mg/L of high calcium quicklime. Approximately 7 mg/L of alum had also been added to improve the settleability of the floc. The water sample was taken from the sedimentation tanks following clarification and prior to recarbonation. At the time of sampling the plant was using both powdered activated carbon (PAC) and potassium permanganate to combat a "chlorinous" taste and odor problem in the water. Approximately 8 mg/L of PAC was added during the recarbonation process following clarification of the softened water.

For comparison three samples of the river water were pretreated. One sample was lime softened with no other chemical additions and two samples were treated by alum coagulation at pH 5.0.

1. Lime Softened. To separate the influence of the added alum and powdered activated carbon in the pretreatment given by the city, a water sample was prepared with lime addition only. The lime used was provided by the treatment plant and had to be slaked prior to addition. 10.4g of the lime was slaked in 300 mL of distilled water and the slurry was added to 80 liters of the river water. One minute of rapid mixing was followed by 45 minutes of slow mixing and several hours were allowed for sedimentation. (In the absence of a coagulant a very fine and poor settling floc was produced).

2. Alum Coagulated. A jar test was conducted on the river water sample to evaluate the response (UVA removal) of the water to varying alum doses when coagulated at pH 5.0. The graph obtained is shown in Figure 111. With this data it was decided to evaluate the influence of 20 mg/L and 80 mg/L of alum doses.

Water samples were coagulated using a rapid mix for approximately 10 seconds and then flocculation for 30 minutes. The pH was adjusted to 5 by the addition of sulfuric acid to the mixed sample following the rapid mix.

All of the samples, including the city water sample, were filtered

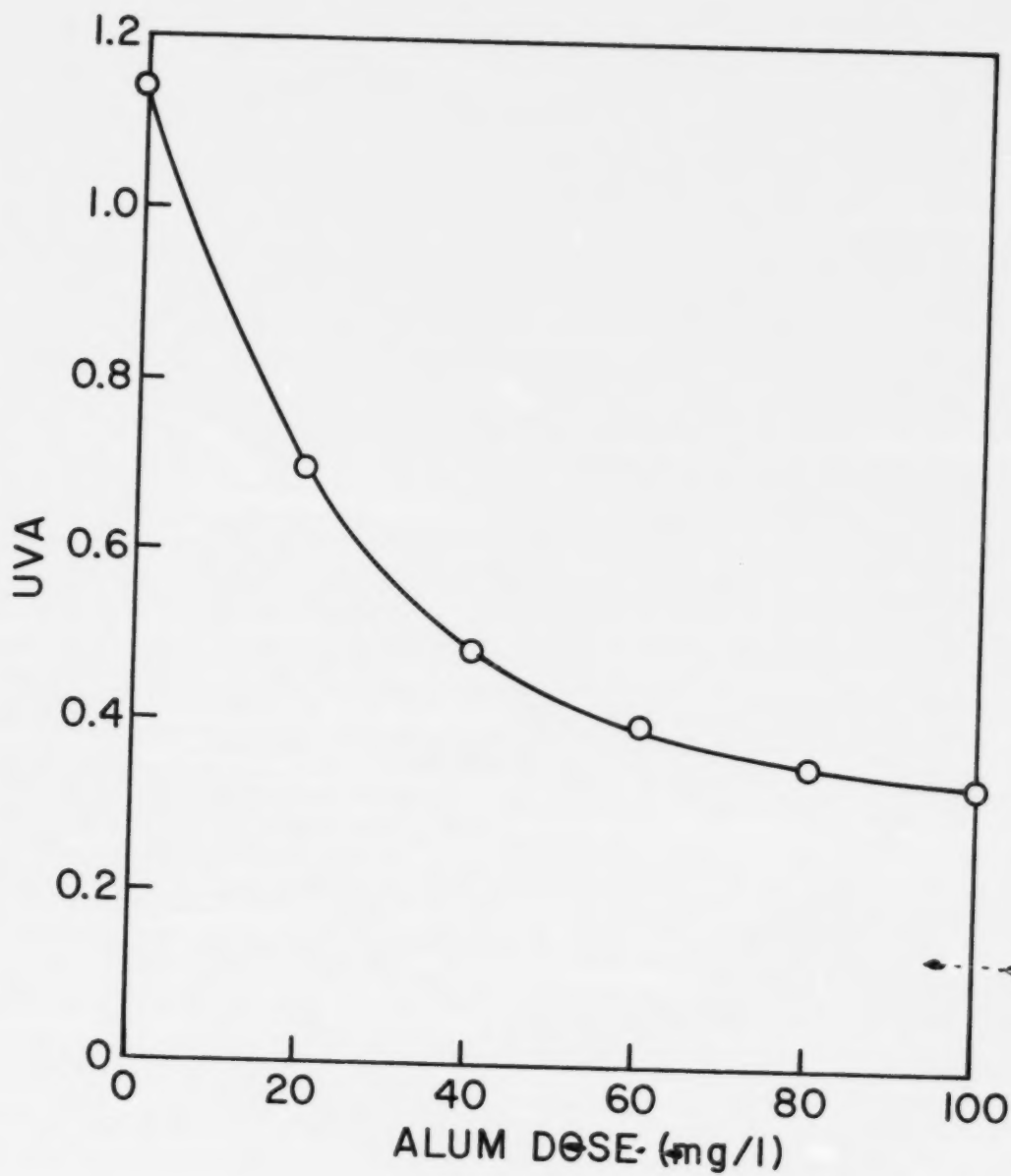


Figure 111. Jar test results employed to determine alum dose for pretreatment.

through a 3 ft. tri-media filter at a loading rate of 2 gpm/ft². Only the sample that was treated exclusively with lime remained a little turbid after filtration. This sample clarified itself in 48 hours, however, and the clarified water was separated from the sediment prior to the column test. All samples were adjusted to pH 7.0 prior to the column test to separate the influence of adsorption pH from the impact of the pretreatment processes.

The pretreated water samples were then fed to 0.9 cm i.d. columns filled with 9 cm of 50x80 mesh activated carbon supported on 2 cm of sand. The columns were operated downflow at a flowrate of 3.5 mL/min for 270 hours. Effluent samples were collected twice daily and influent samples were collected approximately every 3 days.

The results of the study are presented as breakthrough curves for UVA, TOC and THM precursors in Figures 112, 113 and 114, respectively. The resulting curves for the three parameters monitored show excellent correlation in behavioral trends. The results indicate that the lime treated water and the sample receiving 20 mg/L of alum behaved in an essentially identical manner. The city water sample showed a marked improvement in UVA and TOC removal, but an evaluation of THM precursor removal indicated that the city water was only marginally better than lime treatment alone and was very similar to that obtained with the addition of 20 mg/L of alum. In all cases treatment with 80 mg/L of alum gave superior removal and column life was extended significantly.

One may conclude, therefore, that the use of high alum doses at pH 5.0 was more effective for organics removal than the treatment provided by the city treatment plant. However, it is necessary to recognize the different objectives in the treatment processes. Alum coagulation alone does not soften, and if softening is required, an additional process must be employed in conjunction with the alum. It is possible that additional alum in conjunction with lime softening may improve the extent of organics removal and this was evaluated in batch tests as reported in Section 6 of this report.

Interestingly, however, it appears that in spite of powdered activated carbon use in the treatment plant, the THM precursor removal was poor. Even though the TOC and UVA were much reduced, the THM precursor level remained relatively high.

An additional study (Run L) was designed to evaluate the impact of lime dose on activated carbon performance. A river water sample was collected and its hardness was measured. The total hardness was 155 mg/L and calcium was 110 mg/L, both reported as calcium carbonate.

To ensure the appropriate selection of lime dosages for pretreatment, a jar test was run on the river water sample. A wide range of lime dosages was examined in the jar test, the results of which are summarized in Table 19 and Figure 115. In conjunction with the jar test a bar diagram was constructed for the sample (Figure 116). Based on the bar diagram three different lime dosages were calculated according to three different treatment criteria and these are shown in Figure 115 as dashed vertical lines. Because

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TABLE 19. JAR TEST RESULTS FOR LIME DOSE SELECTION - RUN L

Lime Dose (mg/L as CaCO_3)	UVA	Total Hardness* (mg/L as CaCO_3)	pH
100	1.30	98	9.38
130	1.20	85	9.75
160	1.11	86	10.12
200	0.98	94	10.46
230	0.87	101	10.65
260	0.76	99	10.80
300	0.66	108	11.00
0	1.53	155	8.36

*without recarbonation

the dosages calculated from the bar diagram represented three different levels (or objectives) in treatment and because they were evenly spaced on the removal curve, these dosages were chosen for use in column study L. The fourth column used in this study was filtered river water control.

The results of the column study are presented in Figures 117, 118 and 119. The pretreated waters showed increased organics removal as the lime dose was increased, as expected from the jar test results. When the pretreated waters were applied to identical carbon columns, the carbon performance was observed to improve as the lime dose for softening was increased. This result was consistent for TOC, UVA and TTHMFP removals and tends to verify the observed behavior noted above for coagulation: column effluent quality improves with an increasing level of pretreatment.

Even with the highest level of lime addition a relatively poor carbon effluent quality was obtained compared with alum coagulation and this was anticipated. Table 15 and Figure 105 indicated the service life of a carbon bed is related to the adsorption pH as well as the influent water quality, and lime softening was not as effective as was alum coagulation for organics removal.

Batch studies reported in Section 6 of this report indicated that the simultaneous use of alum with lime addition improved the organics removal performance of the softening process. An additional study was, therefore, conducted to evaluate the impact of coagulant addition during lime softening as a pretreatment process for activated carbon. A river water sample was collected that had a total hardness of 158 mg/L as CaCO_3 ($\text{Ca} = 115$ mg/L and $\text{Mg} = 43$ mg/L) and an alkalinity of 143 mg/L as CaCO_3 . Based on these values an excess lime dose of 190 mg/L of lime was calculated to achieve a trial hardness of 80 mg/L.

To ensure the appropriate selection of alum dosages a jar test was run on the water sample. Based on previous experiments dealing with alum use in conjunction with lime, a range of alum dosages from 0 to 50 mg/L was examined. The results of the jar test are summarized in Table 20 and used as a control.

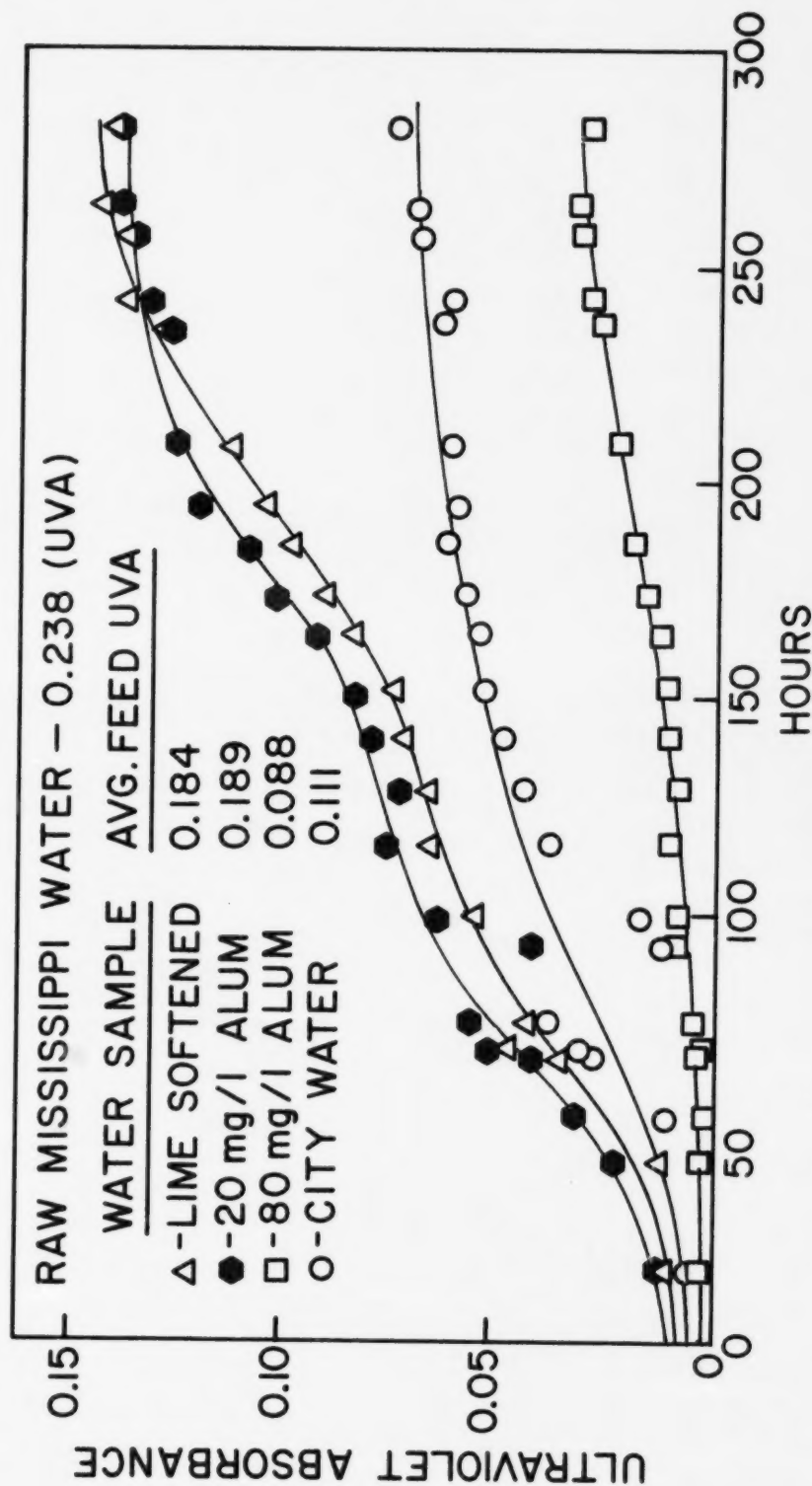


Figure 112. Comparison of UV absorbing organics by GAC following different pretreatments. (See text for treatment conditions). Adsorption pH = 7.0, flowrate = 3.5 mL/minute, EBCT = 1.8 minutes.

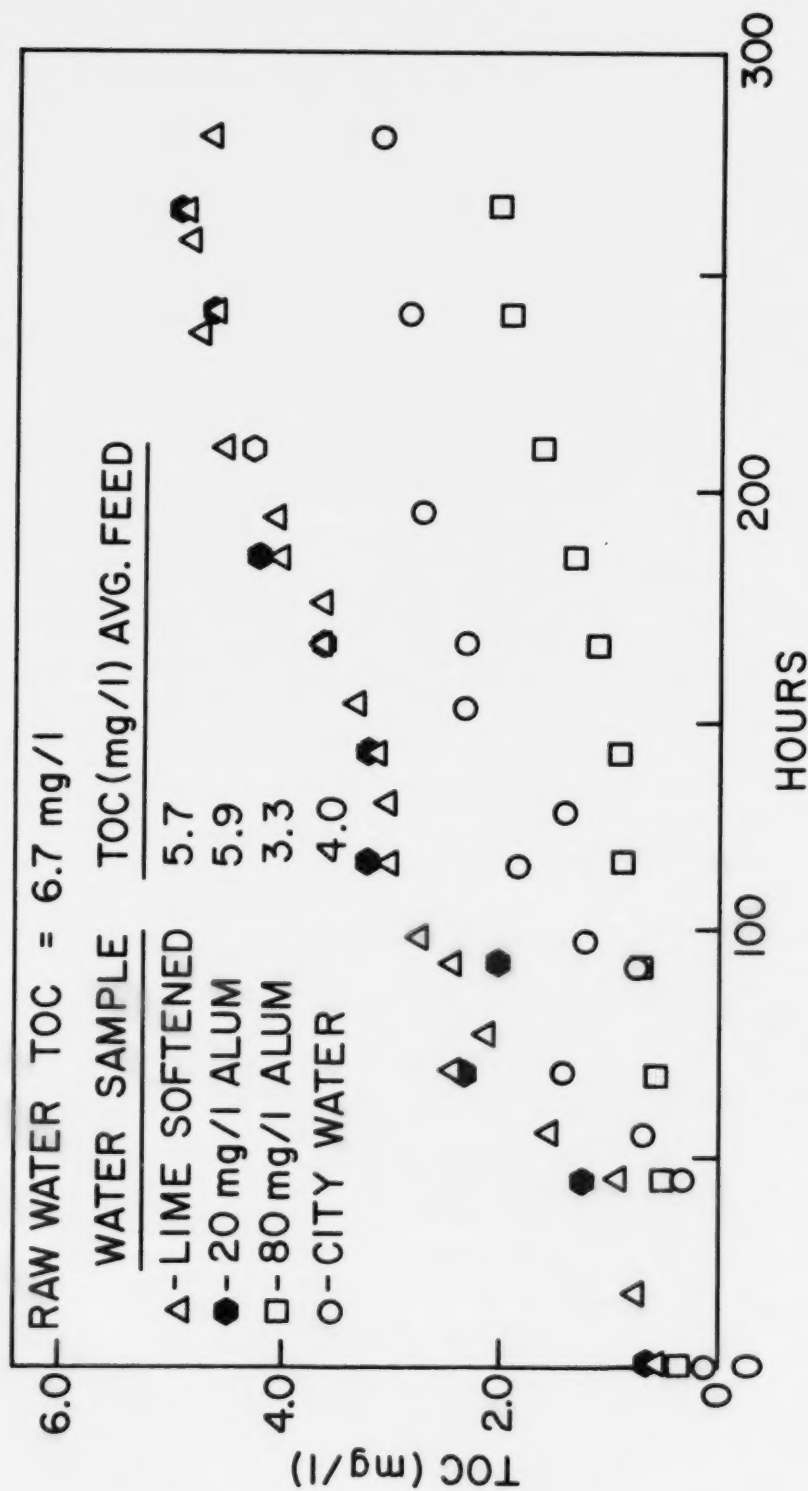


Figure 113. Comparison of TOC removal by GAC following different pretreatments.
(See text for treatment conditions). Adsorption pH = 7.0, flowrate = 3.5 mL/minute, EBCT = 1.8 minutes.

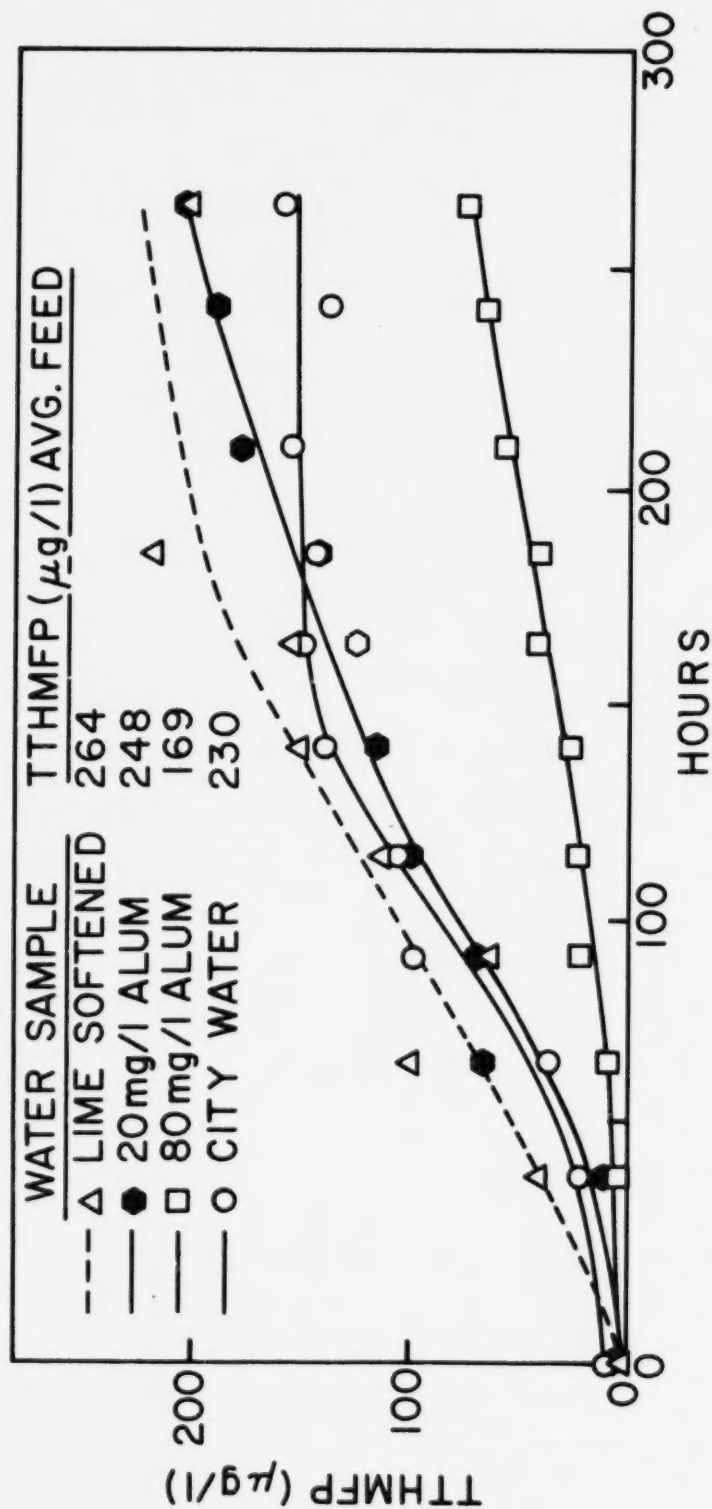


Figure 114. THM precursor removal by GAC following various pretreatments. (See text for treatment conditions). Adsorption pH = 7.0, flowrate = 3.5 mL/minute, EBCT = 1.8 minutes.

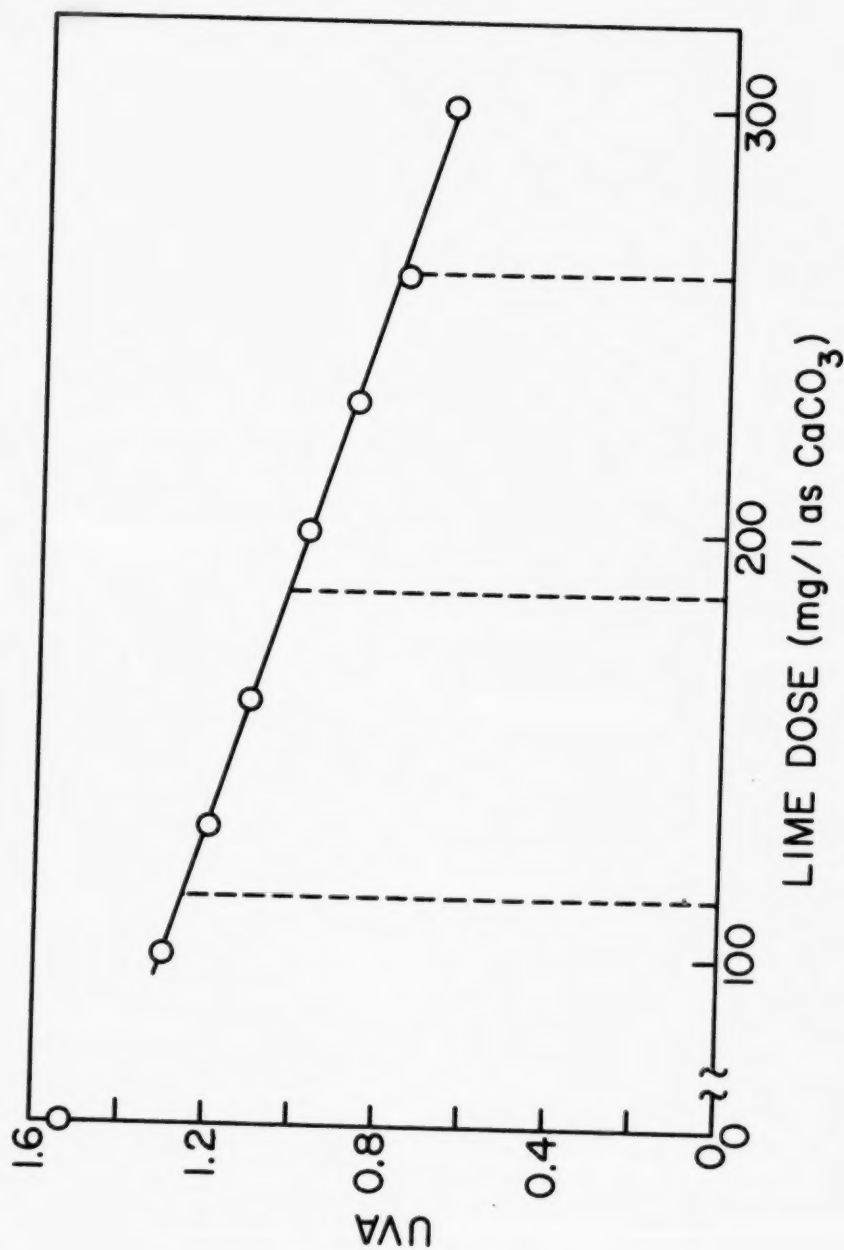
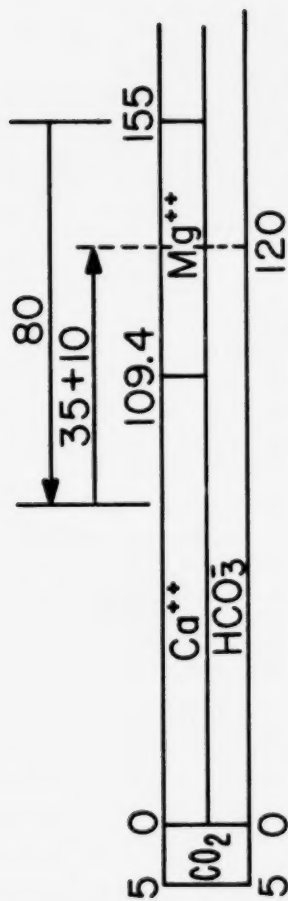


Figure 115. Jar test results for UVA removal from Mississippi River water sample versus lime dose - for Run L.



Calculated Doses mg/L as CaCO₃

Lime Requirement for	Straight Lime	Normal Excess	Max. Removal
CO ₂	5	5	5
Ca	109.4	109.4	109.4
Mg	0	2x10.6	2x45.6
Excess	0	50	60
Total	114.4	185.6	260.6

Figure 116. Bar diagram and dose calculations used for computing lime dosage - Run L.

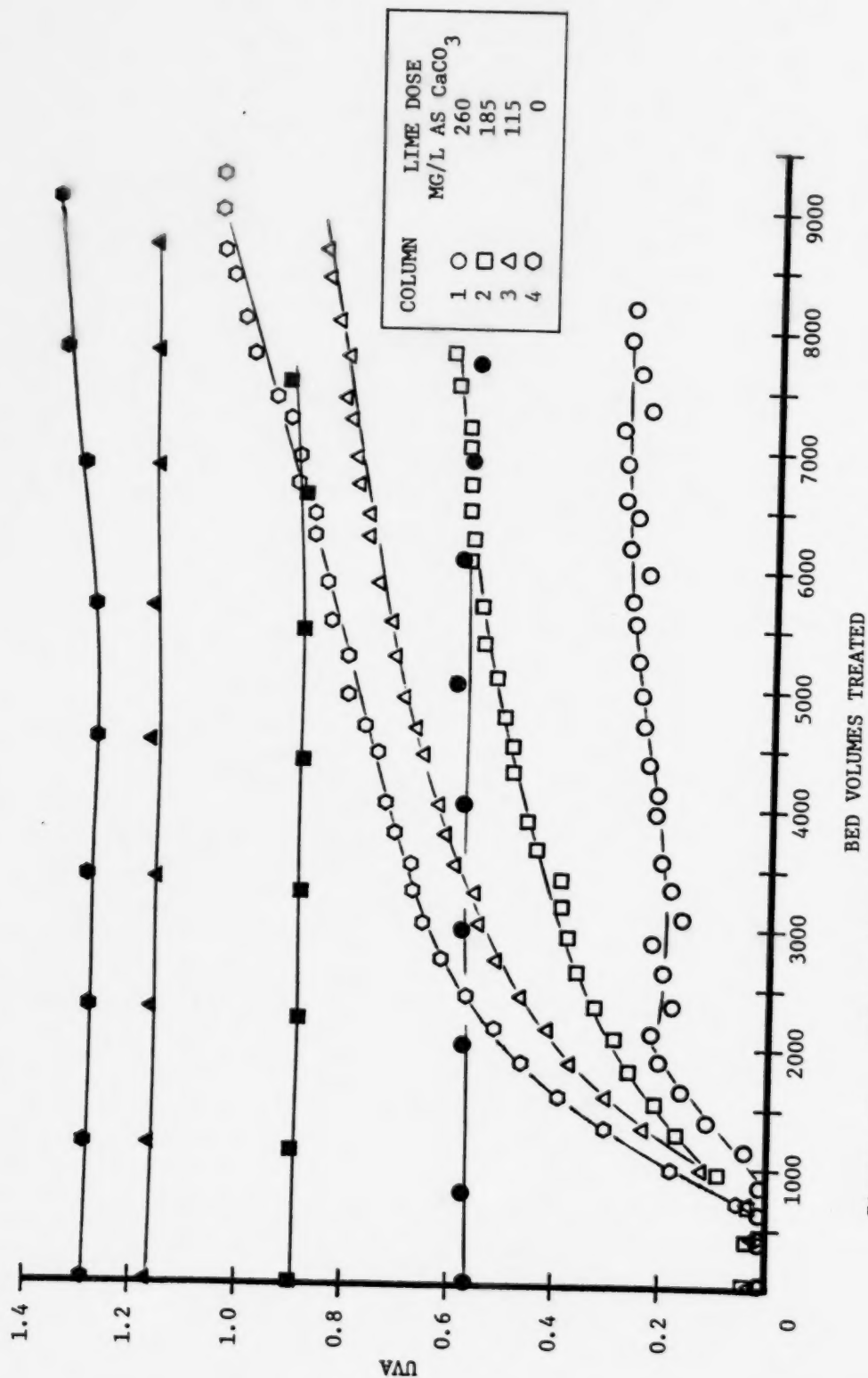


Figure 117. UVA breakthrough for varying lime dose during pretreatment, solid symbols represent column influent

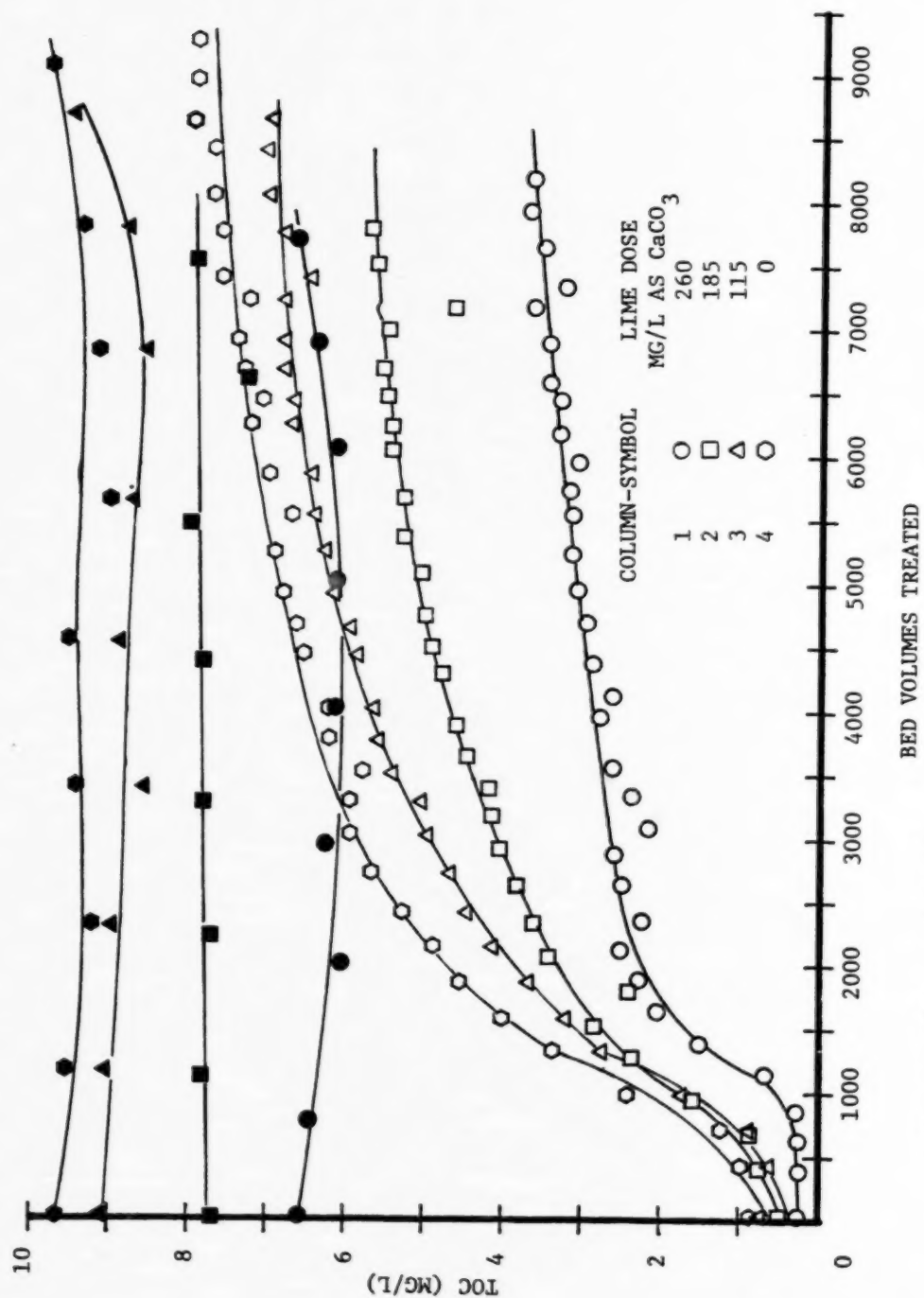


Figure 118. TOC breakthrough for varying lime dose during pretreatment, closed symbols represent column influent

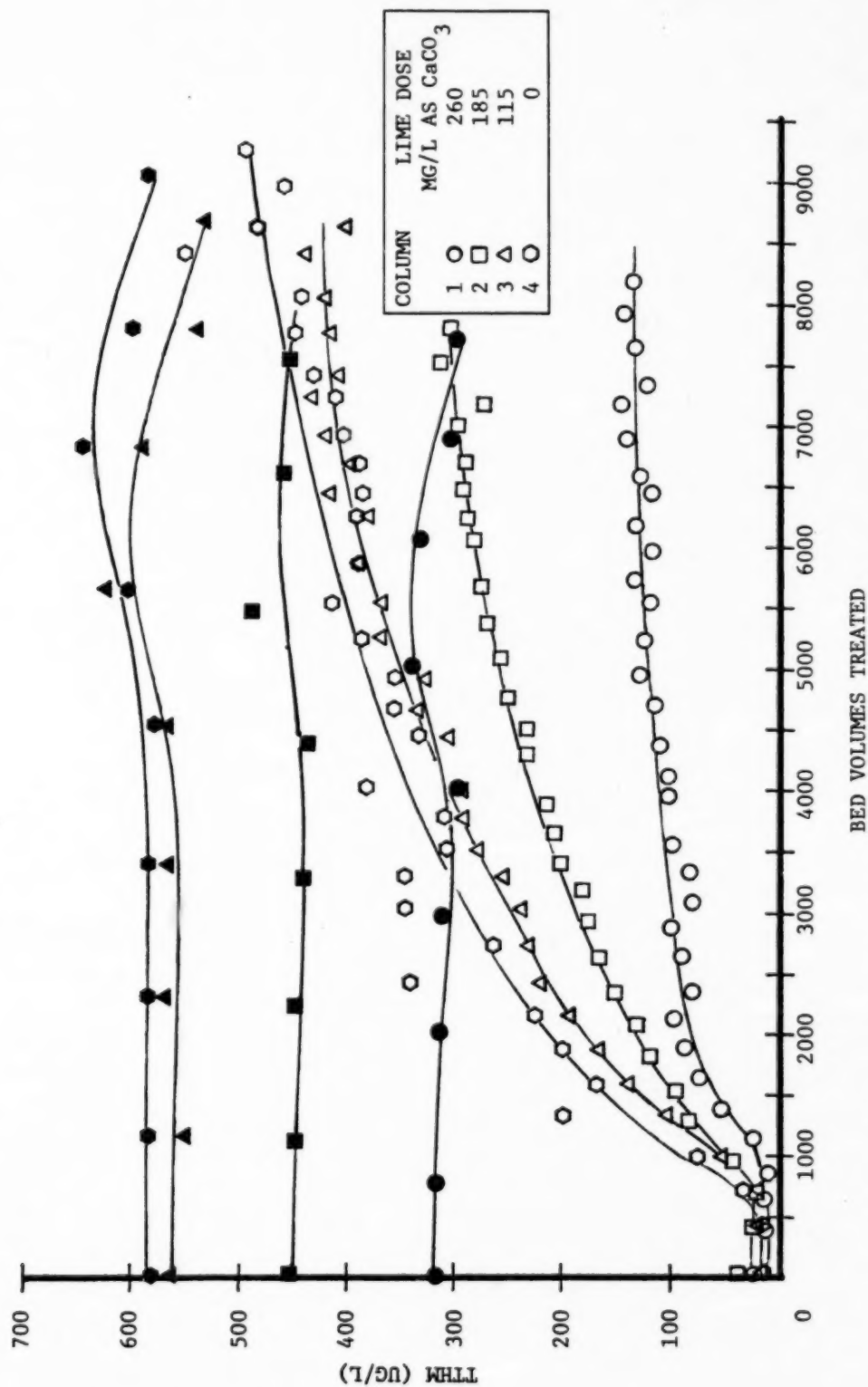


Figure 119. TTHM precursor breakthrough for varying lime dose during pretreatment. Solid symbols represent column influent

TABLE 20. JAR TEST RESULTS FOR ALUM ADDITION DURING SOFTENING-RUN M

Lime Dose mg/L as CaCO_3)	Alum Dose (mg/L)	UVA	Total Hardness* (mg/L as CaCO_3)	pH
190	0	1.20	101	10.45
190	5	0.99	82	10.32
190	10	0.83	73	10.18
190	15	0.76	68	10.05
190	20	0.72	65	9.96
190	35	0.79	74	9.77
190	50	0.93	158	8.28

*without recarbonation

An alum dose of 20 mg/L, along with a lime dose of 190 mg/L, was chosen as the best treatment and two intermediate alum dosages of 3.5 and 8 mg/L were selected to reflect removals between the control and the best treatment case. The results of the column study at an adsorption pH of 7.0 are presented in Figures 120 and 121. The addition of alum resulted in a slight improvement in the performance of the activated carbon columns. However, the improvement was not as marked as expected from the jar test. In the jar test 20 mg/L of alum reduced the UVA by 40%, but when coagulation was practiced on a large scale, only 33% removal was achieved. This may have resulted from differences in mixing conditions.

Analysis of the TOC removal curves in Figure 121 indicated that for a treatment objective of a 1 mg/L effluent TOC, alum pretreatment had little impact upon service life. However, considering an objective of 100 $\mu\text{g/L}$ of TTHM for the chlorination conditions employed, it was apparent that alum extended the precursor breakthrough from 1200 to 1700 bed volumes, an increase of 42%.

Alum is actually used in the Minneapolis water treatment plant as noted above because it assists in the formation of a settleable floc. The alum is, therefore, beneficial in several respects.

The data on carbon performance following softening indicated the same trend observed with coagulation: longer service life results from lower influent organics concentration. To better document this effect a plot was made of the volume of water treated (in bed volumes) before an effluent TOC of 1 mg/L was measured, versus the influent TOC of the pretreated water. The data, taken from the treatment of 3 separate river water samples, is shown in Figure 123. It clearly demonstrates the influence of the feed TOC on column performance and is very similar in character to Figure 105 for alum pretreated waters. These figures are not comparable, however, since column runs were made at pH 7 following softening, whereas Figure 105 is for adsorption at pH 5.0.

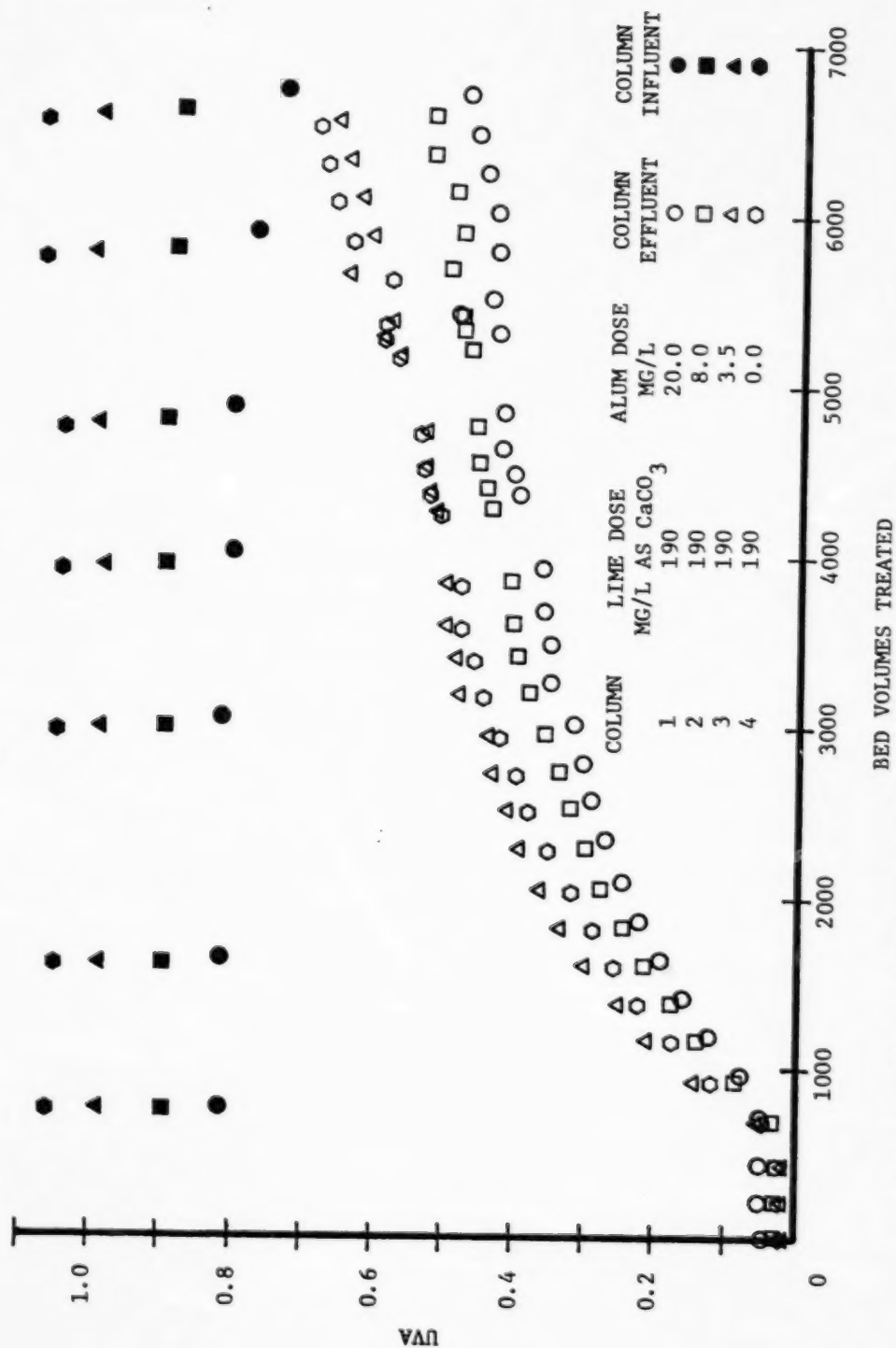


Figure 120. UVA breakthrough following different alum doses during pretreatment

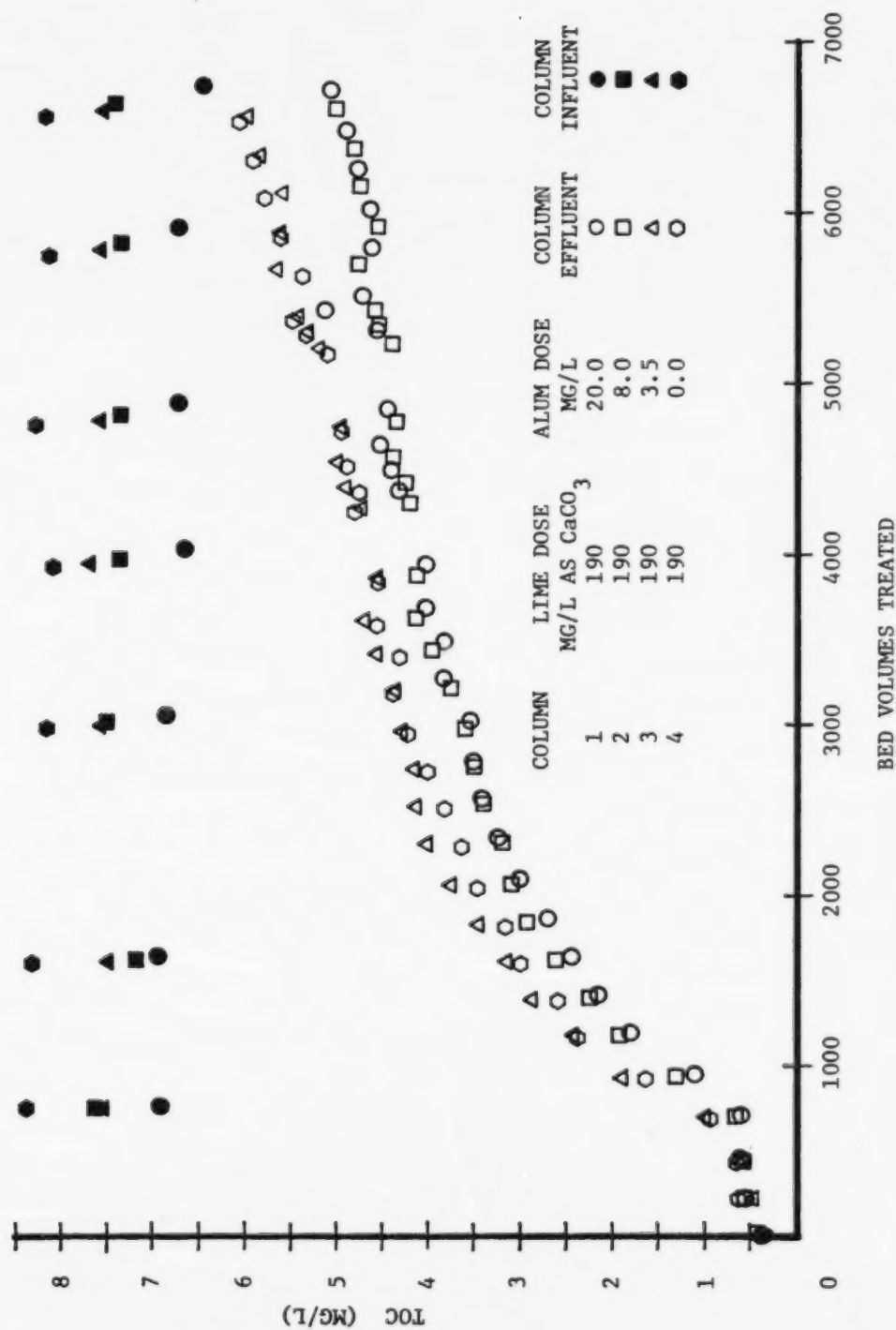


Figure 121. TOC breakthrough following different alum doses during pretreatment.

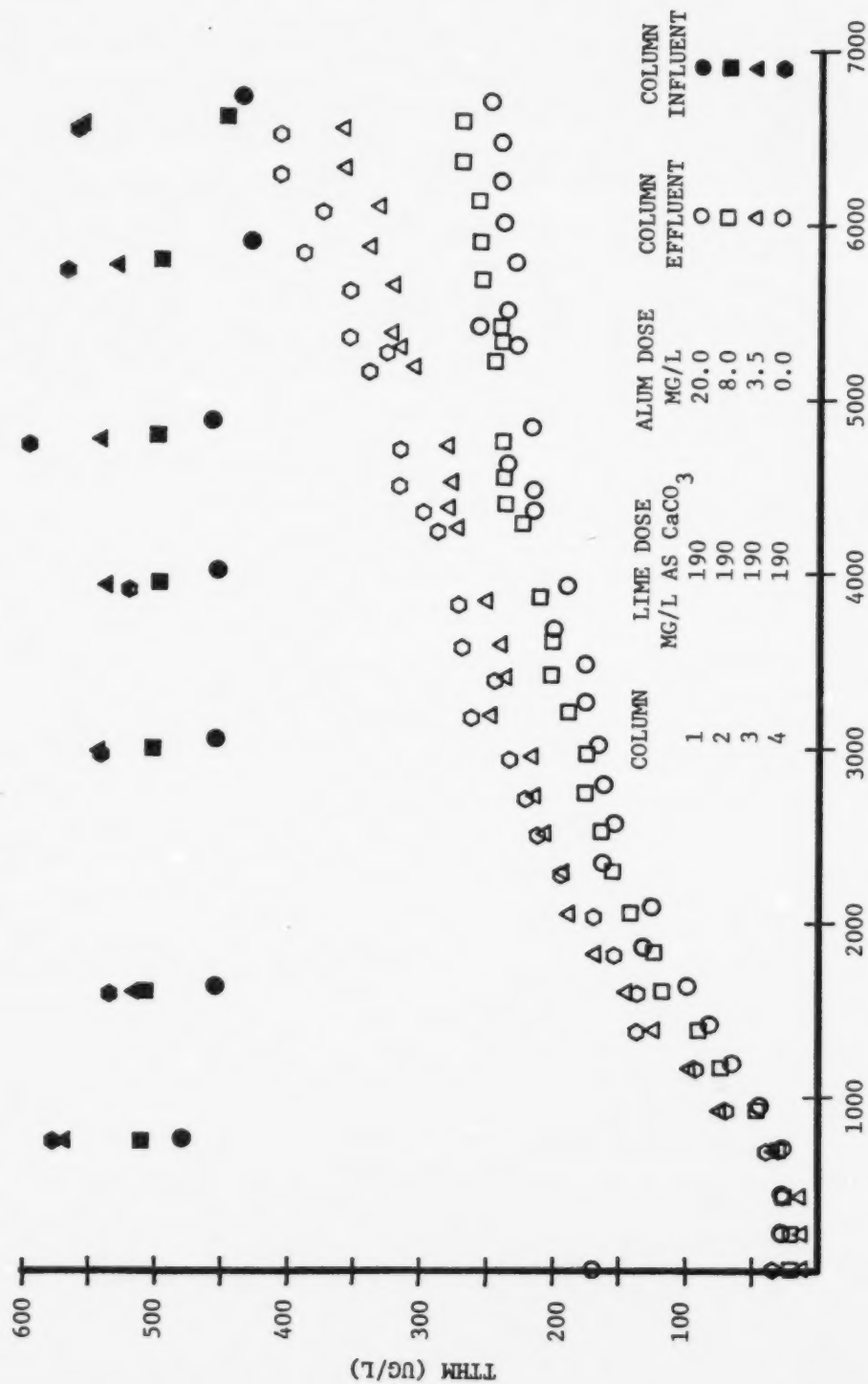


Figure 122. TTHM precursor breakthrough for different alum doses during pretreatment

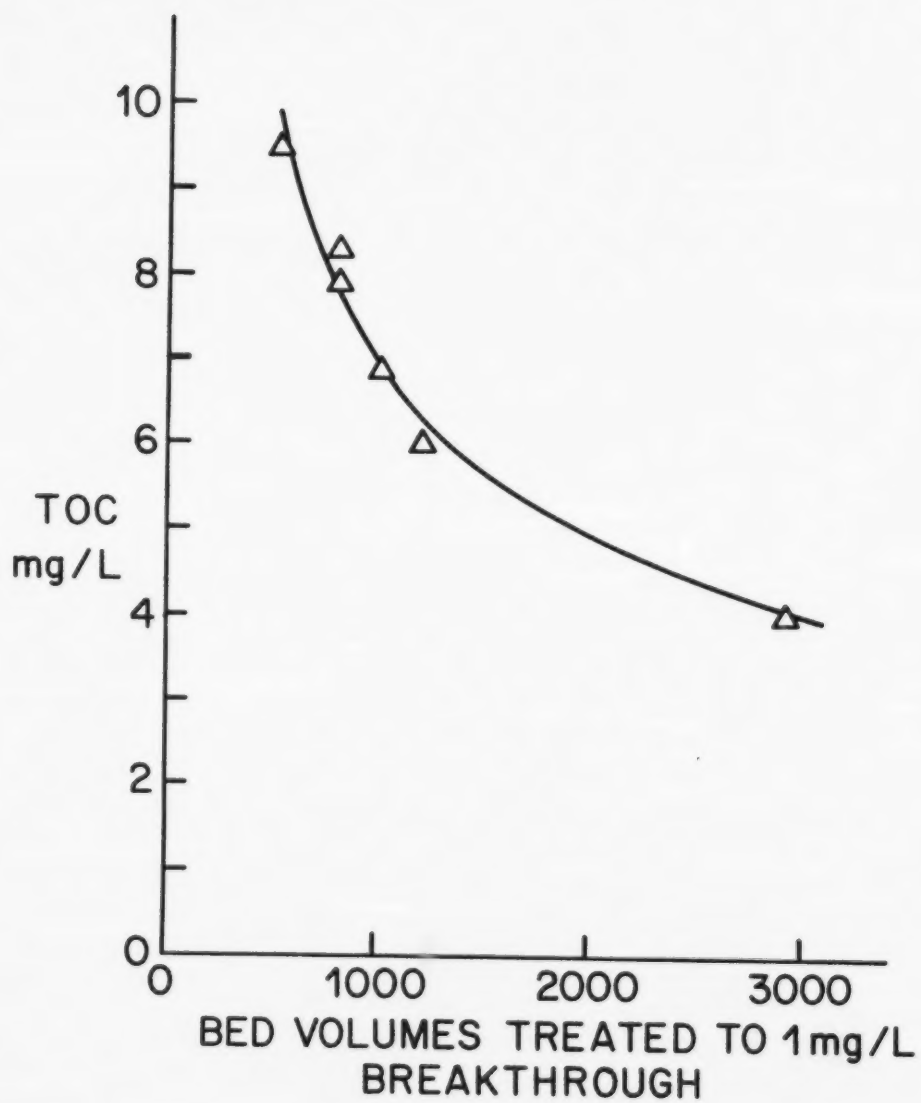


Figure 123. The influence of influent TOC on the performance of GAC (Softening pretreatment, adsorption @ pH 7.0).

Discussion

The column studies were successful in identifying the dynamic adsorption behavior of activated carbon columns for treating river water samples that had received different types of pretreatment. The use of minicolumns to evaluate the impact of alternative pretreatment strategies upon carbon column removal performance is useful. However, the reader may question the significance of these results for full-scale application where biological activity may play a significant role in product water quality, and there is no way to easily estimate the contribution of biological activity in a full-scale system. In the two-week time frame of the minicolumn studies biological activity did not appear to develop to a major extent. This was checked on several occasions with sand-filled columns as controls and the organic content of the column effluents remained essentially constant. In addition, no problems were encountered later in the column studies with headloss development that might be attributable to bacterial growth. However, some biological activity may have developed in the columns because the effluent TOC concentrations never reached the influent levels, and it appeared as if they reached a plateau at a concentration below that of the feed. This was especially apparent in Run T which compared the performance of resins to activated carbon for organics removal from pretreated waters. This run lasted one month and all the columns plateaued at a final concentration that was approximately 90% of the feed concentration.

Although these column studies have their limitations, they provide a useful indication of the relative influence of different operating strategies on the dynamic adsorption behavior of activated carbon, and they complement the studies of other investigators such as Randtke *et al.* (75,95) who evaluated the impact of pretreatments on carbon adsorption using batch equilibria. In addition, mini-columns provide a means of assessing the influence of pretreatment on column behavior and they can be used to identify concepts such as optimum pretreatment as demonstrated in this study.

REFERENCES

1. O'Connor, J., L. Hash, and A. B. Edwards. Deterioration of Water Quality in Distribution Systems. Jour. AWWA, 67:3:113, 1975.
2. Ward, R. F. Organic Fouling of Strongly Basic Anion Exchange Resins. Ph.D. Thesis, Washington University, St. Louis, MO, 1964.
3. Lacey, R. E. and S. Loeb. Industrial Processing with Membranes. Wiley Interscience, New Yoek, 1972.
4. Jobin, R. and M. M. Ghosh. Effect of Buffer Intensity and Organic Matter on the Oxygenation of Ferrous Iron. Jour. AWWA, 64:7:590, Sept., 1972.
5. Oldham, W. F. and E. F. Gloyna. Effect of Colored Organics on Iron Removal. Jour. AWWA, 61:11:610, Nov., 1969.
6. Morris, J. C. Formation of Halogenated Organics by Chlorination of Water Supplies. EPA-600/1-72-002, March, 1975.
7. Stevens, A. A. et al. Chlorination of Organics in Drinking Water. Jour. AWWA, 68:11:615, Nov., 1976.
8. Rook, J. J. Haloforms in Drinking Water. Jour. AWWA, 68:3:168, March, 1976.
9. Preliminary Assessment of Suspected Carcinogens in Drinking Water: Interior Report to Congress. Ofce. Toxic Substances. EPA 17/5/975-2. USEPA, Washington, D.C., Dec., 1975.
10. Tardiff, R. G. and M. Deinzer. Toxicity of Organic Compounds in Water. Proc. WQTC, Univ. of Illinois, IL., 1973.
11. AWWA Committee Report. Organics Removal by Coagulation: A Review and Research Needs. J. AWWA, pp. 588-603, October, 1979.
12. Shapiro, J. Concentration of Volatile Substances in Aqueous Solution and Production of Water Free of Organics by Freezing Out. Anal. Chem., 39:280, Feb., 1967.
13. Shapiro, J., Concentration of Humic Acids in Natural Waters. Fractional Solidification, in Purification of Inorganic and Organic Materials, M. Zief, Ed., Vol. 2, Marcel Dekker, N.Y., 1969.
14. Semmens, M. J. and T. K. Field. Coagulation--Experiences in Organics

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- Removal. J. AWWA, pp. 476, August, 1980.
15. Weber, W. J. Physicochemical Processes for Water Quality Control, Wiley Interscience, N.Y., 1972.
 16. Schnitzer, M. The Chemistry of Humic Substances. Environmental Biogeochemistry. Vol. 1 (U. O. Nriagu, Ed.), Ann Arbor Science, Ann Arbor, MI, 1976.
 17. Schnitzer, M. and S. U. Khan. Humic Substances in the Environment. Marcel Dekker, New York, 1972.
 18. Shaw, D. J. Introduction to Colloid and Surface Chemistry. Butterworths, Boston, 1970.
 19. Sridharan, N. and G. F. Lee. Environ. Sci. and Technol. 6, 12, 1031, 1972.
 20. Tatsumoto, M., W. T. Williams, J. M. Prescott, and D. W. Hood. Jour. Mar. Res. 19, 89 1961.
 21. Chapman, G. and A. C. Rae. Nature, 214, 627, 1967.
 22. Williams, P. M. and A. Zirino. Nature, 204, 462, 1964.
 23. Semmens, M. J. and G. Ocaras-Sanchez. Removal of Specific Trace Organics from Water During Chemical Coagulation. AIChE Symp. Series No. 167, Vol. 73, pp. 42, 1976.
 24. Gjessing, E. T. Physical and Chemical Characteristics of Aquatic Humus. Ann Arbor Science, Ann Arbor, MI, pp. 42, 1976.
 25. Morris, J. C. EPA-600/1-75-002. March, 1975.
 26. Hullet, D. A. and S. J. Eisenreich. Determination of Free and Bound Fatty Acids in River Water by High Performance Liquid Chromatography. Anal. Chem. 51 (12), pp. 1953, 1979.
 27. Hullet, D. A. The Characterization of Biologically Important Organic Acids in the Upper Mississippi River. M.S. Thesis, University of Minnesota, 1979.
 28. Sturm, W. and J. J. Morgan. Chemical Aspects of Coagulation. Jour. AWWA, 54:971, 1962.
 29. Referenced in Gjessing, E. T., Physical and Chemical Characteristics of Aquatic Humus, Ann Arbor Science, Ann Arbor, MI, 1976.
 30. Eisenreich, S. J., D. Rastetter, E. C. Yost, M. R. Hoffmann, W. J. Maier, Trace Metal Transport Phases in the Upper Mississippi River, in Particulates in Water. Chapter 7, M. Kavanaugh and J. O. Leckie (Ed.), Advances

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- in Chemistry Series, American Chemical Society, Washington, D.C. (1980).
31. Maier, W. J., C. A. Macko, S. J. Eisenreich, M. R. Hoffmann, Ultrafiltration Characterization of Aquatic Organics. Proc. AICHE, Feb., 1980.
 32. Chian, E. S. K. and F. DeWalle, Env. Eng. Division, J.A.S.C.E., 1974.
 33. Leenheer, J. A. and E. W. D. Huffman, Jr. Classification of Organic Solutes in Water by Using Macroreticular Resins. Journal Research, U.S. Geol. Surv. 4, (6) pp. 737, 1976.
 34. McGhee, T. J. Heuristic Analysis of Lime-Soda Softening Processes, Jour. AWWA.
 35. Gjessing, E. T. and G. F. Lee. Fractionation of Organic Matter in Natural Waters on Sephadex Columns. Env. Sci. and Tech. 1:631, 1967.
 36. Field, T. and M. Semmens. Coagulation: Experiences in Organics Removal. J. AWWA (8), pp. 476, 1980.
 37. AWWA Coagulation Committee Report. Organics Removal by Coagulation: A Review and Research Needs. J. AWWA (10) pp. 588, 1979.
 38. Black, A. P. et al. Stoichiometry of Coagulation of Color-causing Organic Compounds with Ferric Sulphate. Jour. AWWA, 55 (10), pp. 1347, 1963.
 39. Bowie, J. E., Jr. A Comparison of Aluminum Sulfate and Activated Carbon for Organic Color Removal from Groundwaters. Master's Thesis, Mississippi State University, State College, Miss., 1975.
 40. Shaw, D. J. Introduction to Colloid and Surface Chemistry. Butterworth, Boston, 1970.
 41. Black, A. P. and D. G. Willems. Electrophoretic Studies of Coagulation for Removal of Organic Color. Jour. AWWA, 53:4:438, April, 1961.
 42. Edzwald, J. K. Coagulation of Humic Substances. Presented at AICHE Mtg., Atlanta, GA., 1978.
 43. Hall, E. S. and R. F. Packham. Coagulation of Organic Color with Hydrolyzing Coagulants. Jour. AWWA, 57:9:1149, Sept., 1965.
 44. Zuckerman, M. M. and A. H. Molof. High Quality Reuse Water by Chemical-Physical Wastewater Treatment. Journal W.P.C.F. 42 (3), pp. 437, 1970 and Discussion by W. Weber, pp. 456.
 45. Chow, K. and M. M. David. Compounds Resistant to Carbon Adsorption in Municipal Wastewater Treatment. J. AWWA 69, pp. 555, 1977.
 46. Mullins, R. L., J. S. Zogorski, S. Aittubbs, and G. D. Allgeier. The

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47. Eisenreich, S. J., M. R. Hoffmann, D. Rastetter, E. Yost and W. J. Maier. Metal Transport Phases in the Upper Mississippi River. In Particulates in Water, Advances in Chemistry Series No. 189, pp. 135, 1980.
48. Stevens, A. A., D. R. Seeger, J. DeMarco and L. Moore. Removal of Higher Molecular Weight Organic Compounds by the Granular Activated Carbon Adsorption Unit Process. Proceedings Practical Application of Adsorption Techniques in Drinking Water, Reston, Virginia, April 30, 1979.
49. DeWalle, F. B. and E. S. K. Chair. Removal of Organic Matter by Activated Carbon Columns. J.A.S.C.E., Vol. 100, No. EE5, pp. 1089, 1974.
50. Kaiser, K. L. and J. Lawrence. Polyelectrolytes: Potential Chloroform Precursors. Science, Vol. 196, pp. 1205, June, 1977.
51. DeMarco, J., A. A. Stevens and D. J. Hartman. Application of Organic Analysis for Evaluation of Granular Activated Carbon Performance in Drinking Water Treatment. Presented ACS Chemical Congress, Las Vegas, Nevada, August 24-29, 1980.
52. Popalisky, J. R. and F. W. Pogge. Detection and Treatment of Organic and Taste and Odor Compounds in the Missouri River. AWWA Annual Meeting, Denver (Session 27), June 17, 1971.
53. Suffet, I. H. Monitoring Aspects of the Adsorption Unit Process for Drinking Water. Ch. 24, Activated Carbon Adsorption from the Aqueous Phase, Vol. 2 (Michael J. McGuire and Irwin H. Suffet, Ed.), Ann Arbor Science, Ann Arbor, MI, 1980.
54. Glazer, E. R., B. Silver and I. H. Suffet. Computer Plots for the Comparison of Chromatographic Profiles. Jour. Chromatog. Sci., 15:22, Jan., 1977.
55. Stevens, A. A., D. R. Seeger, C. J. Slocum, and M. M. Domino. Gas Chromatographic Techniques for Controlling Organic Removal Unit Processes. Presented AWWA Water Quality Technical Conference, Miami Beach, Dec., 1980.
56. Suffet, I. H., L. Brenner, J. Coyle, and P. R. Cairo. Evaluation of the Capability of Granular Activated Carbon and XAD 2 Resin to Remove Trace Organics from Treated Drinking Water. Env. Sci. & Tech., 12 (12), pp. 1315, 1978.
57. Taflin, C., Minneapolis Water Treatment Plant, Personal communication (1980).
58. Nalco Laboratories, Chicago, Illinois, Personal communication (1980) W. M. Krier.

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59. Edzwald, J. K., J. D. Haff, and J. W. Boak. Polymer Coagulation of Humic Acid Waters. Jour. of the Environmental Engineering Division, 103, EE 6, 989 (Dec. 1977).
60. Keys, R. O. and R. Hogg. Mixing Problems in Polymer Flocculation. AIChE Symposium Series, 75, 63 (1978).
61. Haff, J. D. Removal of Humic Acid Using Alum and Synthetic Polyelectrolytes. Jour. AWWA, 70:9:520 (1978).
62. Black, A. P., F. B. Birkner, and J. J. Morgan. Destabilization of Dilute Clay Suspensions with Labeled Polymers. Jour. AWWA, 57, 12, 157 (1965).
63. Nalco Chemical Company. Clay Polymer Coagulation. Technifax: Water Treatment Chemicals TF-104.
64. Baylis, J. R., Silicates as Aids to Coagulation, Jour. AWWA 29, 9, 1335 (1937).
65. Stumm, W., H. Huper and R. L. Champlin. Formation of Polysilicates as Determined by Coagulation Effects. Env. Sci. & Tech., Vol. 1, No. 3, 221 (March 1967).
66. Benedek, A., McMaster University, Canada, Personal communication, July 1979.
67. Jekel, M. R., The Influence of Chemical Parameters on the Removal of Humic Acids by Aluminum and Ferric Salts, Unpublished Engler-Bunte-Inst., University of Karlsruhe, Germany (1980).
68. Mangravite, F., Arco Performance Chemical Co., Personal communication, 1980.
69. Macko, Christine, Organics Removal by Ion Exchange, Ph.D. Thesis, University of Minnesota, Mpls., 1980.
70. Ward, T. M. and F. W. Getzen. Influence of pH on the Adsorption of Aromatic Acids on Activated Carbon, Env. Sci. & Tech., p. 64, 4 (1) 1970.
71. Ward, T. M. and F. W. Getzen. A Model for the Adsorption of Weak Electrolytes on Solids as a Function of pH. Part 1. Carboxylic Acid - Charcoal Systems, J. Colloid and Interface Sci., p. 441, 31 (4) 1962.
72. Snoeyink, V. L., W. J. Weber, H. B. Mark, Jr. Sorption of Phenol and Nitrophenol by Active Carbon, Env. Sci. & Tech., p. 918, 3 (10), 1969.
73. Coughlin, R. W. and R. N. Tan. Role of Functional Groups in Adsorption of Organic Pollutants on Carbon, Water 1968, Chem. Eng. Progress Symp. (90) Vol. 64, pp. 209.

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74. Myers, A. L. and R. R. Zolandz. Effect of pH upon Multicomponent Adsorption from Dilute Aqueous Solution.
75. Randtke, S. J. and C. P. Jepsen. Chemical Pretreatment for Activated Carbon Adsorption. J. AWWA, 73 (8), p. 411, 1981.
76. Schnitzer, M. and H. Kodana. Montmorillinite: Effect of pH on its Adsorption of a Soil Humic Compound, Science 153:70 (1966).
77. Black, A. P. and R. F. Christman. Characteristics of Colored Surface Waters, J. AWWA, 55 (6), p. 753, 1963.
78. Lee, M. C., V. L. Snoeyink, and J. C. Critterden. Activated Carbon Adsorption of Humic Substances, Journal AWWA, 73 (8), p. 440, 1981.
79. Sontheinier, H. and D. Maier. Studies on the Improvement of Water Treatment Technology in the Lower Rhine Region, Gas Wasserfach, Wasser/Abwasses 113 (4), p. 187 (1972).
80. McCreary, J. J. and V. L. Snoeyink. Characterization and Activated Carbon Adsorption of Several Humic Substances, Water Research 14:151 (1980).
81. Ward, R. F. Organic Fouling of Strongly Basic Anion Exchange Resins. Washington Univ., Sever Inst. Tech., St. Louis, MO, 1964.
82. Boening, P. H., et al. Activated Carbon Versus Resin Adsorption of Humic Substances. Journal AWWA 72 (1) 54, 1980.
83. Gaurtlett, R. A. A Comparison Between Ion Exchange Resins and Activated Carbon for the Removal of Organics from Water. Water Res. Tech. Rept., Trio. Medmenham Lab., Medmenham, England (1975).
84. Wood, P. R. and J. Demarco. Effectiveness of Various Adsorbents in Removing Organic Compounds from Water. In Activated Carbon Adsorption of Organics from the Aqueous Phase, Vol. 2, M. J. McGuire and I. H. Suffet (Ed.), Ann Arbor Science, 1980.
85. Semmens, M. J. A Review of Factors Influencing Selectivity of Ion Exchange Resins for Organic Anions, Adsorption and Ion Exchange Symp. AIChE, 152:71:214 (1975).
86. Diamond, R. M. and D. C. Whitney. Resin Selectivity in Dilute to Concentrated Aqueous Solutions. Ion Exchange, Vol. 1, (J. A. Marinsky, Ed.), Marcel Dekker, N.Y., 1966.
87. Gregory, J. and M. J. Semmens. The Selectivity of Strongly Basic Anion Exchange Resins for Organic Anions, Env. Sci. & Tech., 8, p. 834, 1974.
88. Criswell, C. D., et al. Comparison of Macroreticular Resins and Activated Carbon as Solvents, J. AWWA, 69 (12), p. 669 (1977).

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89. Symons, J. M., et al. Removal of Organic Contaminants from Drinking Water Using Techniques other than Granular Activated Carbon Alone. A Progress Report, U.S. Govt. Printing Office, 657-060/5301 (1979).
90. Weber, W. J., et al. Synthetic Adsorbents and Activated Carbons for Water Treatment: Overview and Experimental Comparisons. J. AWWA, 73 (8) 420 (1980).
91. Rook, J. J. and S. Evans. Removal of Trihalomethane Precursors from Surface Water Using Weak Base Resins. J. AWWA 71 (9), p. 520 (1979).
92. Evans, S. and T. F. Maalman. Removal of Organic Acids from Rhine River Water with Weak Base Resins. Environ. Science & Tech., 13 (6) 741 (1979).
93. Hinrichs, R. L. and V. L. Snoeyink. Sorption of Benzenesulfonates by Weak Base Anion Exchange Resins. Water Research 10, 79 (1976).
94. Abrams, I. M. Removal of Anionic Surfactants from Liquids. Patent No. 3 232 867, U.S. Patent Office (1966).
95. Randtke, S. J., et al. Removal of Soluble Contaminants by Lime-Soda Softening. Submitted to J. AWWA Sept. 1981.
96. Cohen, J. M., Rourke, G. A. and R. L. Woodward. Natural and Synthetic Polyelectrolytes as Coagulant Aids. J. AWWA 50:4:453 (1958).
97. Walles, W. F. Role of Flocculant Molecular Weight in the Coagulation of Suspensions, J. Colloid and Interfacial Science, 27:4:797 (1968).
98. Ayers, K. Removal of Organic Material from Mississippi River Water by Coagulation with Alum and Ferric Sulphate. M. S. Thesis, University of Minnesota, 1980.
99. Idelovitch, Wastewater Reuse by Biological-Chemical Treatment and Groundwater Recharge, J. WPCF 50:12:2723 (1978).
100. Steiner, J. and J. E. Singley. Methoxychlor Removal from Potable Water. J. AWWA 71:5:284 (1979).
101. Young, J. S. and P. C. Singer. Chloroform Formation in Public Water Supplies: A Case Study. J. AWWA 71:2:87 (1979).
102. Evans, G. C. and C. F. Gerald, Chem. Eng. Prog., 49, 135 (1953).
103. Letterman, R. D., R. R. Sama, and E. J. DiDominico. Direct Filtration Using Polyelectrolyte Coagulants. J. AWWA 71:6:332 (1979).
104. Caskey, J., et al. Effect of Polyacrylamide Molecular Structure on Flocculation Efficiency, AIChE Symp. Series 70, 144, 120 (1974).

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105. Carr, R. L. Water and Sewage Works, R-72, 1972.
106. Michaels, A. S. Aggregation of Suspensions by Polyelectrolytes. Ind. and Eng. Chem., 46, 7, 1485 (1954).
107. Keinath, T. M. Modeling and Simulation of Performance of Adsorption Contactors. In Mathematical Modeling in Environmental Engineering, 8th Annual Workshop AEEP, Nassau, Bahamas, 1972.
108. Chu, J. E., J. Kalil, and W. A. Wetteroth. Mass Transfer in a Fluidized Bed. Chem. Eng. Prog. 49, 141 (1953).
109. Pfeffer, R., and J. Happel, AIChE J., 10, 605 (1964).
110. Fan, L. T., Y. C. Yang, and C. Y. Wen, AIChE J. 3, 482 (1960).
111. Moore, Leown, Personal communication, Feb. 1982.
112. Weber, W. J. Discussion of reference 44. See reference 44.

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